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PRODUCTION OF SECOND-GENERATION BIOFUELS FROM WOODY BIOMASS

By

Sanjeev Kumar Gajjela

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PRODUCTION OF SECOND-GENERATION BIOFUELS FROM WOODY BIOMASS

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Increased research efforts have recently been accelerated to develop liquid transportation fuels from bio-oil produced by fast pyrolysis. However, these bio-oils contain high levels of oxygenated compounds that require removal to produce viable transportation fuels. A variety of upgrading technologies have been proposed, of which catalytic hydroprocessing of the raw bio-oil has appears to have the best potential due to the fact that no fractionation of the bio-oil is required prior to treatment.

The objective of this research was to apply two-stage catalytic hydroprocessing to bio-oil with heterogeneous catalysts to produce hydrocarbon fuels. To achieve this objective seven catalysts were initially compared in first-stage hydrotreating reactions. The result of the comparison of the seven hydrotreating catalysts showed that the MSU-1 catalyst had the significantly highest yield at 38 wt%, had the highest H/C ratio, and reduced oxygen adequately. The MSU-1 catalyst had an energy efficiency of 80%, reduced acid value by 45% and water content by 78%. Higher heating value was doubled by the hydrotreating process of raw bio-oil.

Three catalysts were compared as second-stage hydrocracking catalysts. All liquid organic products produced by the catalytic reactions were compared with regard to yield and chemical and physical qualities. Results from these experiments showed that the MSU-2 catalyst had the significantly highest yield at 68 wt%; oxygen value was significantly lower than for the compared catalysts at zero percent. MSU-2 also produced the lowest amount of char at 3.5 wt%. Additionally, MSU-2 produced a high volume of methane gas as a byproduct, with a high value for utilization for production of process heat. A study of reaction time optimization found that best results from application of MSU-2 were for the shortest reaction time of 1 h. This short reaction time is important to reduce hydroprocessing costs. Simulated distillation of hydrocarbon mix results in distribution of these by fuel weights with gasoline comprising 37%, jet fuel 27%, diesel 25% and heavy fuel oil 11%.The energy efficiency of the hydrocracking of first-stage stabilized bio-oil with MSU-2 catalyst was 93.61%.

DEDICATION

The author would like to dedicate this research to Satyam Gajjela (Father), Savithri Gajjela (Mother), Swetha Gajjela (Spouse) and Raja Rao Chintaginjala (Bro-in-Law).

ACKNOWLEDGEMENTS

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LIST OF TERMS

HDS: hydrodesulfurization

HDO: hydrodeoxygenation

HT: hydrotreating

HC: hydrocracking

DHA: detailed hydrocarbon analysis

FTIR: Fourier transform infrared spectroscopy

^{1}H-NMR: proton nuclear magnetic resonance

CHAPTER I

AN INTRODUCTION TO CATALYTIC HYDROPROCESSING OF BIOMASS

DERIVED FAST PYROLYSIS BIO-OIL

1.1   Overview

1.1.1   U.S. Energy demand and renewable energy solution

Worldwide energy consumption of fossil fuels increased several fold in the last century. In the next thirty years, the U.S. energy consumption in the transportation sector is estimated to increase to over 30 quadrillion Btus (quads) according to the latest 2010 annual energy outlook report released from Energy Information Administration (EIA) [1]. Typical U.S. transportation sector consumption fluctuated between 20 to 30 quads from 1980-2008 periods as shown in Figure 1.1. Based on the rate experienced over this period consumption is estimated to increase to approximately 40 quads by the year 2035 [1].

For the transportation sector, liquid fuels are of primary interest. The major concerns associated with this sector are diminishing oil reserves, rapid fluctuations in oil prices and environmental effects due to the combustion of petroleum fuels [2, 3]. Replacement of a percentage of petroleum derived fuels with biofuels will both reduce greenhouse gas emissions and increase fuel supply as we approach peak petroleum oil production [4-6]. The U.S. Department of Energy (DOE) and the U.S. Department of Agriculture (USDA) recently published a report that conceives of replacing 30%of current petroleum consumption with biofuels by the year 2030 [7].
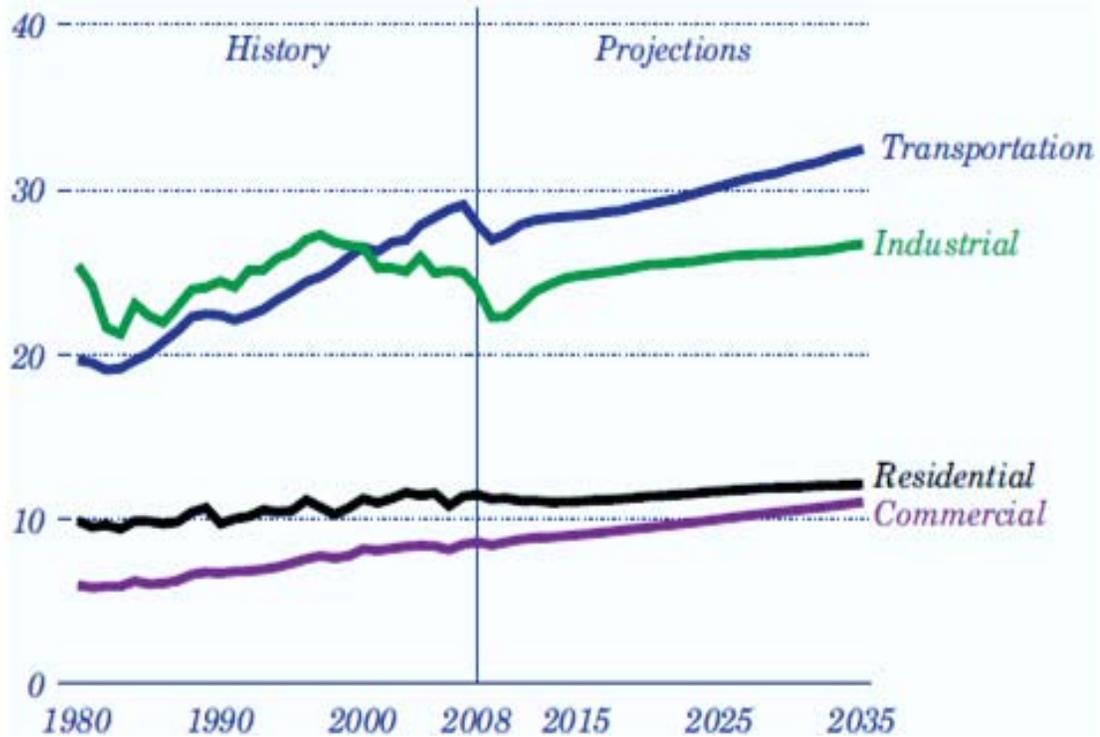
Figure 1.1   Delivered energy consumption by sector, 1980-2035 in quads adapted from ref [1].

The U.S. has large amounts of biomass in the form of forest, agricultural crops and land residues. From forest land and agricultural land alone it can produce 1.3 billion dry tons of biomass per year, enough to produce biofuels to meet more than one third of current demand for transportation fuels [7]. As shown in Figure 1.2, it is currently estimated that renewable energy sources supply only 6% of the total U.S. energy supply. The consumption of biomass in the U.S. for fuels is expected to increase several fold in near future with improved research and development of biomass derived fuels [7].
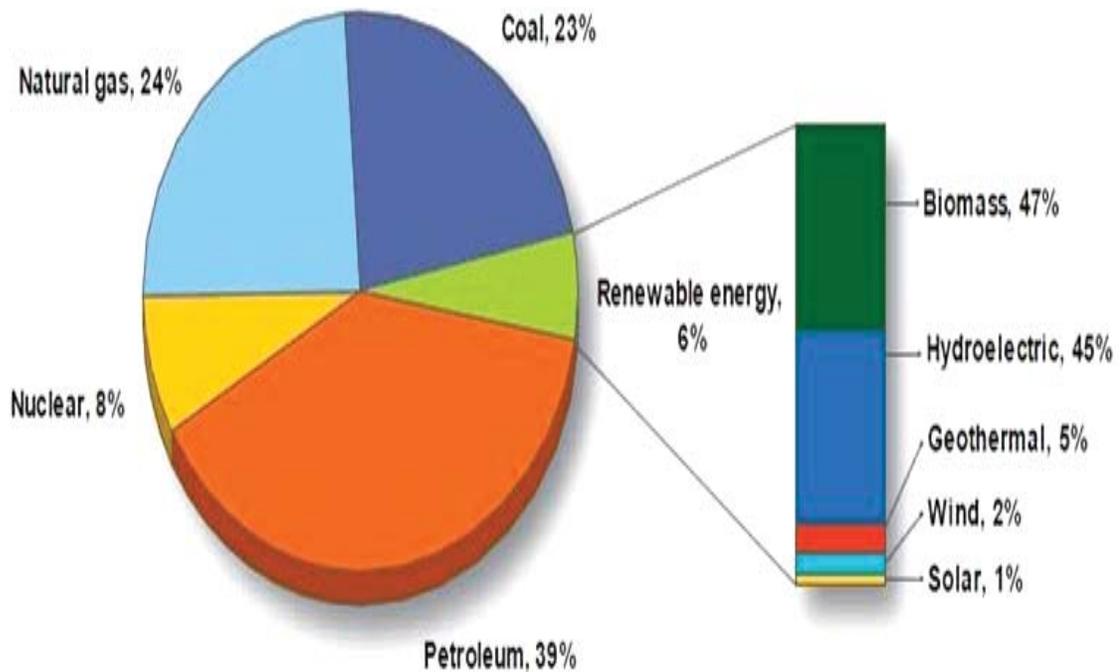
Figure 1.2   United States energy consumption by fuel type adapted from ref [7].

1.2   Classification of biofuels

1.2.1   First-generation biofuels

First-generation biofuels are mostly produced from food sources and oils derived from plants [8]. The most common examples are bio-diesel (from soybean, rapeseed, sunflowers, etc.), bio-ethanol and bio-butanol (from starch and sugar, etc). These raw materials are primarily derived from stocks suitable for food purposes. There is concern that as the production of biofuels from these food sources increases, that they cannot be supplied in the quantities required by the transportation sector and simultaneously maintain consistent food prices. Several industries have commercialized these first-generation biofuels and the capacity of these refineries appears to be much lower than typical petroleum refinery units (100 MWth compared to several GWth's in conventional petroleum refineries) [9].

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1.2.2   Second-generation biofuels

To resolve the issues associated with first-generation biofuels, researchers are seeking to utilize non-edible renewable energy feedstocks for the production of what are now termed second-generation biofuels [8]. One potential alternative is biomass feedstock [10-12]. Lignocellulosic biomass is widely distributed and less expensive than food-based feedstocks, and biofuels can be more sustainably produced. lignocellulosic biomass feedstocks include of wood/plant residues, agricultural residues, forest residues, waste wood residues and others. Biofuels emit negligible amounts of sulfur, nitrogen and ash upon combustion. The conversion of lignocellulosic biomass is considerably more complex than the processing of food-based feedstocks to fuels. Despite this complexity there are considerable efforts aimed at production of fuels from conversion of lignocellulosic biomass [6]. Producing biofuels from biomass will assist in reducing reliance on petroleum, both domestic and foreign sources. In addition, the food chain will not be influenced by the utilization of lignocellulosic biomass. There are numerous ways to convert biomass to biofuels; major routes are non-biological processes [13] that include thermochemical conversion as shown in Figure 1.3 [12, 14]. Thermochemical conversion refers to a non-catalytic process and applies high temperature to convert biomass by processes such as gasification and pyrolysis. Gasification applies high temperature (800 to 1200 $^{\circ}$C) to convert biomass to gases such as H_2, CO, CO_2 and CH_4 [15, 16]. The main objective is to produce a synthesis gas (syngas) with equal proportions of CO and H_2. Syngas can be utilized as a feedstock from which to produce various fuels by Fisher-Tropsch (FT) and water-gas shift reactions as shown in Figure 1.3 [17]. Syngas products include methanol, ethanol, lubricants, dimethyl ether, FT-diesel and synthetic petroleum [17].
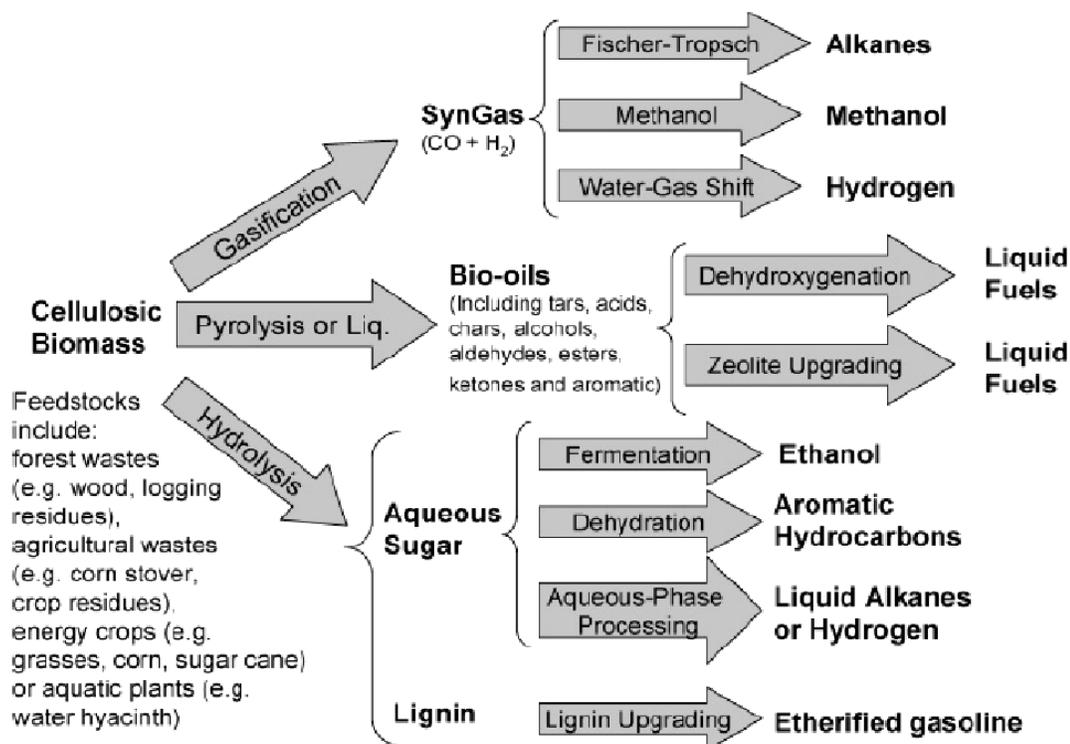
Figure 1.3   Strategies for production of fuels from lignocellulosic biomass adapted
              from ref. [17, 18].

1.3   Bio-oil production by fast pyrolysis

Pyrolysis processes are performed in the absence of oxygen at atmospheric pressure and at high temperatures ranging from 450 to 550 ^{o}C. Char is the main product developed from the traditional slow pyrolysis process in which biomass is slowly heated to a temperature between 300 to 400 ^{o}C [11, 12]. By contrast the fast pyrolysis applied to biomass feedstocks is defined as the rapid (<0.2 s) thermal decomposition of biomass to vapors followed by rapid condensation of the produced vapors to a liquid. The liquid product is known as bio-oil or pyrolysis oil, and it is considered to be a promising route for the biomass conversion to second-generation fuels [6, 9, 12, 13, 19, 20]. The byproducts formed during fast pyrolysis of biomass feedstocks are solid char and non-condensable gases. Typical yields of bio-oil and byproducts of the pyrolysis process are

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given in Table 1.1. Bio-oil liquid yield from fast pyrolysis of biomass ranges from 60 to

75 wt%, solid char from 12-15 wt% and non-condensable gases are nearly 13 wt% dry

weight depending on the applied pyrolysis process conditions and biomass feedstock

type.

Table 1.1   Typical yields from fast pyrolysis of biomass (dry wood basis) [11].

Products	Yields, dry wt%
Liquid bio-oil	65-75
Solid char	12-13
Non condensable gases	13-15

Biomass feedstocks for fast pyrolysis production of bio-oil can be of any type

with differences of yield obtained that depend on the feedstock type pyrolyzed. Fast

pyrolysis must be applied to small biomass particles (1-3 mm) for rapid thermodynamic

heat transfer through the particle at high temperature during the pyrolysis process [11,

21].

Bio-oil, while difficult to ignite, burns as steadily as No. 2 fuel oil after ignition.

Researchers have found that support fuels are helpful to assist in ignition and for

smoother burning. Bio-oil emits higher particulate matter and CO_2 during combustion.

However, compared to petroleum fuels, SO_x emissions are much lower and most research

indicates that, for most applications, NO_x emissions are also lower [6]. The only current

commercial products utilizing bio-oil are the liquid smokes utilized as food flavorings on

a relatively large scale. Raw bio-oil has been test combusted in diesel engines, both neat

and as an emulsion containing diesel fuel. Raw bio-oil has also been tested in turbines

and Stirling engines for the production of electricity. With the exception of the Stirling

engine test researchers detected engine corrosion, deposits or wear and tear [6]. The other major alternatives for the liquid bio-oil are that it can be catalytically upgraded to transportation fuels or it can be used for the production of high value-added chemicals and co-products [6, 9, 11, 21].

Solid char can be combusted in the pyrolysis process a combustible product to provide the pyrolysis heat. Non-condensable gases can be re-routed to the pyrolysis reactor to use as processing heat or for drying the biomass [6, 12].

If not consumed in the fast pyrolysis process the char byproduct can be utilized for firing boilers, as an agricultural soil amendment, for the production of activated carbon or reinforcing fillers in plastic and rubber goods. [22].

1.4   Bio-oil characteristics

Bio-oil produced from fast pyrolysis of biomass is a dark brown, free flowing liquid with a pungent phenolic odor. Extensive reviews on fast pyrolysis of biomass and bio-oil characteristics have been reported by Bridgwater and Peacocke [12]; Mohan et al. [11]; Elliott [5], and Huber et al. [17]. Table 1.2 summarizes the major functional group components present in e raw bio-oil.

Table 1.2   Component families in the crude bio-oil [14, 23].

Components	Wt%
acetic acid	15.3
acetone	5.3
other ketones	21.8
other acids and esters	10.8
hydroxyacetaldehyde	10.6
other aldehydes	8.7
phenols	8.2
alcohols	11.6
ethers	0.9
levoglucosan	3.9
others	1.3
non-identified	1.6
Total	100

Bio-oil properties vary with feedstock type and applied pyrolysis conditions but woody biomass typically produces a mixture of 15.3 wt% acetic acid, 5.3 wt% acetone, 21.8 wt% other ketones, 10.8 wt% other acids and esters, 10.6 wt% hydroxyacetaldehyde, 8.7 wt% other aldehydes, 8.2 wt% phenols, 11.6 wt% alcohols, 0.9 wt% ethers, 3.9 wt% levoglucosan and 3 wt% miscellaneous and non identified compounds [12, 19] as shown in Table 1.2. Most of the compounds present in bio-oil are highly oxygenated compounds.

Table 1.3 compares the physical and chemical properties of bio-oil to those of petroleum diesel fuel. The presence of a high percentage of oxygenated compounds (40-45 wt%) is the main reason for bio-oil negative properties such as low volatility, high density (1.2 g/mL), lower heating value (17 MJ/kg) of less than half the value of

conventional fuel oil (43 MJ/kg), corrosiveness, immiscibility with fossil fuels and tendency to polymerize during storage and transportation. Bio-oils also are highly acidic with a typical pH between 2 to 3 and an acid value of 94. Bio-oil viscosity is about 7.15 cSt which is almost three times higher than petroleum diesel fuel (2.6 cSt). Bio-oils have a very high flash point compared to fuel oil but they are combustible at high temperatures with or without addition of solvents. Sulfur content is negligible in bio-oil because biomass contains very low quantities of sulfur. But in petroleum diesel, sulfur present approximately about 0.05 wt% level.

Table 1.3   Comparison of raw bio-oil and petroleum diesel physical and chemical properties [17].

property	Bio-oil	Diesel[1]
Viscosity (cSt) at 40 ^{o}C	7.15	2.6
Density (g/ml)	1.15-1.2	0.94
pH	2.3-2.5	~7
Acid value (mg KOH/g)	94	0.0
Water content , wt%	23.5	0.05 max
Heating value (MJ/kg)	17.0	43.0
Ash content, wt%	~0.1	0.1
Flash point (^{o}C)	40-65	<40
Oxygen content, wt%	~43.5	1.0
S	<0.01	~0.05

[1]Standard specification for diesel fuel oils -ASTM D975

1.5   Bio-oil upgrading

Various upgrading technologies have been proposed to improve the fuel properties of bio-oil. Bio-oil upgrading approaches are mainly divided into two types.

Physical upgrading or non-reactive methods applied for the partial improvement of bio-oil fuel properties.

1.5.1 Catalytic upgrading of bio-oil

The second approach to bio-oil upgrading is catalytic reactive upgrading. Of the methods tested to date catalytic hydrotreatment appears to be the most promising route. This bio-oil hydrotreatment is similar to the hydrodesulfurization (HDS) technique applied for sulfur removal in petroleum refineries [5]. Typically, harsh conditions (250-400 $^{\circ}$C and 1000-2000 psig of hydrogen pressure are required to obtain hydrocarbons as a product from the petroleum refinery process. This process is known as hydrodeoxygenation (HDO). HDO removes the oxygenated compounds hindering the bio-oil miscibility with fossil fuels in the form of H_2O and CO_2. Accordingly, upgrading by application of HDO diminishes the undesirable bio-oil properties, instability and high viscosity, which are induced by phenolic and ether (methoxy) groups. This is accomplished by producing a hydrocarbon mix with saturated C-C bonds. A simplified schematic HDO chemical reaction is shown in Eq. 1.1 below.

$$-(CHO)- \ + \ H_2 \quad \longrightarrow \quad -(CH)- \ + \ (H_2O, CO_2, CH_4, CO) \qquad \text{(Eq. 1.1)}$$
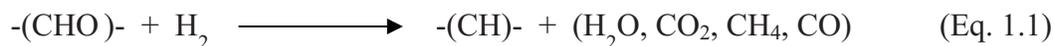
Currently, HDO of bio-oil has employed well-known hydrotreating catalysts traditionally applied in the petroleum industry HDS process. Examples are sulfided $CoMo/Al_2O_3$ (CoMo/Al), sulfided $NiMo/Al_2O_3$ (NiMo/Al), noble metal catalysts (Pd/C, Pt/C, Pt/Al, Ru/C, & Ru/Al) and zeolites material (ZSM-5, MCM-41 and SUZ-4). During hydroprocessing of bio-oil, several reactions take place such as hydrodeoxygenation, decarboxylation, decarbonylation, hydrogenation, hydrogenolysis, hydrocracking and polymerization reactions leading to the formation of coke on the catalyst [5, 14, 17]. An

extensive in-depth review of bio-oil hydroprocessing research was published by Elliott in 2007 [5].

Elliott et al. [25-27] studied upgrading of fast pyrolysis of bio-oil in a fixed-bed continuous reactor at 350 $^{\circ}$C with sulfided CoMo/Al catalyst in the presence of 2000 psig of hydrogen gas. Hydrocarbon product yield was 23 wt% with 4-6 wt% of oxygen content. During the experiments a tar-like product plugged the catalyst bed and the catalyst was heavily coked. Based on this result researchers hypothesized that a two-stage process may reduce the bio-oil polymerization that causes the tar formation and subsequent catalyst coking. They tested this hypothesis by applying a first-stage hydrotreating to stabilize the bio-oil and a second-stage hydrocracking to convert the stabilized bio-oil to hydrocarbons. Elliott et al. [25-27] utilized CoMo/Al to catalyze the reactions required for both stages. During the first-stage hydrotreating, a mild hydrogenation or mild hydrotreating (HT) was performed at a relatively low temperature below 270 $^{\circ}$C. Full HDO of bio-oil required that the hydrocracking (HC) second-stage temperature be above 300 $^{\circ}$C. Elliott et al. [23, 25] patented this two-stage HDO bio-oil upgrading process in 1989. In subsequent research on the influence of mild hydrotreating on bio-oil characteristics it was shown that heat did not increase treated bio-oil viscosity as is the case for raw bio-oils [28-30].

Sheu et al. [31] performed a wide range of bio-oil hydrotreating experiments in a packed-bed reactor at temperatures between 350-450 $^{\circ}$C at 50-100 bar pressure and weight hourly space velocities (WHSV) between 0.5-3.0 h^{-1}. Several hydrotreating catalysts were employed ranging from noble metal catalysts such as Pt/Al$_2$O$_3$/SiO$_2$ to the conventional HDS catalysts such as sulfided CoMo, nickel-tungsten on gamma alumina (Ni-W/γ-A1$_2$O$_3$) and NiMo. Researchers concluded that the NiMo catalyst was superior

for HDO of bio-oil in terms of product oil yield and stability of the catalyst when compared to the others tested.

Elliot et al. [29] further studied the HDO of bio-oils with a bench scale two-stage packed-bed continuous reactor to test additional catalysts beyond the originally tested CoMo. Both NiMo and CoMo catalysts were supported on γ-A1$_2$O$_3$ support. In addition the researchers tested additional liquid hourly space velocities (LHSV) in an attempt to optimize this variable for these catalysts. The researchers applied a first-stage temperature of 150-200 ^{o}C for the stabilizing hydrotreating step and a second-stage hydrocracking step at temperatures of 300-400 ^{o}C for complete HDO. The researchers concluded that the maximum deoxygenation rate was dependent on a LHSV of 0.1 h^{-1}. However, complete deoxygenation of bio-oil during these experiments was not achieved due to early deactivation of the hydrotreating catalysts.

Zeolites are various types of crystalline alumino-silicates that occur in nature and are also synthesized [33]. Zeolites are effective hydrogenating catalysts in addition to being proven cracking catalysts. More than 100 varieties of zeolites are currently available with new candidate zeolites added monthly [17]. Zeolites, such as ZSM-5, HZSM-5 and MCM-41 in various forms have been applied to catalyze pyrolysis vapors to attempt to produce liquid hydrocarbons suitable for fuels. The catalysts proved to be ineffective due to their rapid coking [32, 34-37]. Upgrading bio-oil over zeolites produced liquid hydrocarbons directly suitable as fuels but the yields were low and the catalysts deactivated rapidly due to coking of bio-oil components [38, 39].

In an effort to elucidate the HDO mechanisms during bio-oil hydroprocessing several researchers employed oxygenated model compounds rather than raw bio-oil. The use of a limited number of chemical compounds was thought to simplify the

identification of appropriate catalysts, reaction rates and key mechanisms [40-43]. The model compounds tested were furans, phenolic derivatives, methylarylethers and carboxylic acids. Ferrari et al. [43] studied HDO of model compounds to determine the influence of metals impregnation order for CoMo and MoCo carbon supported catalyst efficacy. Researchers chose 4-methylacetophenone to represent the bio-oil ketone family, ethyl deaconate to represent the ester family and guaiacol to represent bio-oil phenolic compounds. However, early deactivation and incomplete deoxygenation occurred, preventing elucidation of reactions in relation to catalyst characteristics.

Sharma and Bakshi et al. [32] tested HZSM-5 as a hydrocracking catalyst to attempt to hydroprocess model compounds representing bio-oils. Their fixed-bed micro reactors were operated at atmospheric pressure and at temperatures ranging from 370 to 410 $^\circ$C. Experiments were performed with various hydrogen donating solvents such as tetralin, steam and methanol. The upgraded products contained large amounts of benzene, toluene, xylene and other aromatic hydrocarbons. Phenolics were reduced, but not eliminated by these treatments. The researchers concluded that this method of solvent application as a hydrogen donor had only marginal effect on model compound conversion to hydrocarbons.

Following bio-oil mild hydrotreating substituted phenols make up a larger portion of the bio-oils. Phenols from the bio-oils of pine contain 3-methoxy groups along with a wide variety of other functional groups in the 1- position. Phenols and substituted phenols yield the corresponding cyclohexanes when hydrogenated and the pungent odor associated with phenols will not be present after hydrogenation. Hydrogenation of phenolic compounds will have the greatest impact on the chemical and physical properties of bio-oils.

Gandarias et al. [44] studied HDO of phenol as a model compound representing bio-oil phenolic compounds by comparing reduced and presulfided forms of NiMo and nickel-tungsten (NiW) catalysts on γ-Al$_2$O$_3$ in a continuous reactor. Product distribution and catalyst stability were tested versus changes in feed composition, solvent type and catalyst pretreatment. Experiments were performed at temperatures between 200 to 350 ^{o}C with H$_2$S and H$_2$ catalyst pretreatment. Results were mixed for NiMo, which produced a product with low aromatic content but its catalytic activity was higher than for NiW. It was concluded that presulfidation was not an effective pretreatment for NiMo. This result was attributed to the fact that the MoS$_2$ active phase was not enabled due to the presence of P. By contrast, presulfided NiW had higher isomerization activity and produced an increased yield of higher aromatics, i.e. higher conversions of methyl-cyclopentane. However, researchers also found that the NiW catalyst was rendered less stable due to presulfiding.

Zhang et al. [45] studied the HDO of fast pyrolysis bio-oil in the presence of CoMo. Effects of reaction time, temperature, and partial hydrogen pressure were determined. Experiments were performed in a 500 mL batch reactor at 360, 375, and 390 ^{o}C. Researchers concluded that as reaction time increased, the deoxygenation rate increased. However, after 20 min the deoxygenation rate decreased due to deactivation of the catalyst. They also concluded that hydrogen pressure had little effect on the deoxygenation of bio-oil. Full deoxygenation of bio-oil was not achieved in these experiments.

Wildschut et al. [46] employed first-stage HDO to bio-oil with precious metal catalysts (Ru/Al$_2$O$_3$, Ru/C, Ru/TiO$_2$, Pd/C and Pt/C) in a 100 mL batch reactor at 350 ^{o}C and 200 bar hydrogen pressure for 4 h. Researchers concluded that ruthenium or platinum

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on carbon catalysts provided equally superior yield and deoxygenation, reducing oxygen content from 40 to 6 wt%. Product yields were 35 wt% water, 23 wt% light hydrocarbons, 17 wt% gases, 18 wt% heavy hydrocarbons and 7 wt% solids. Researchers concluded that prolonged reaction time led to decreased product yields and increased oxygen content which may be due to the gasification of the products and depolymerization of solids. Complete deoxygenation of bio-oil was not achieved in this process.

Biomass Technology Group (BTG) in collaboration with University of Twente developed a novel process known as high-pressure thermal treatment (HPTT) for partially upgrading the bio-oil to allow its co-processing with a standard refinery stream. In the HPTT process bio-oil was thermally treated at temperatures of 300-340 ^{o}C with lengthy residence times at 140-250 bar [47-49]. The products obtained after this treatment were an oil phase (~79 wt%), an aqueous phase (~18 wt%) and a gas phase (5 wt%) with a small amount of char. The product oil phase had improved HHV (from 14.1 to 28.2 MJ/kg) and reduced oxygen content (40 to 23 wt%) were reported. However, the HPTT process required long residence times for bio-oil upgrading and the final oil phase product was immiscible with conventional heavy refinery stream products [47-49].

It is clear that successful application of the HDO bio-oil upgrading process needs further research for attaining a hydrocarbon mix suitable for direct combustion as a drop-in fuel or for blending with standard petroleum fuels. To achieve partial and complete deoxygenation of bio-oil, heterogeneous catalysts with suitable reaction characteristics are necessary. This thesis mainly focuses on finding a suitable heterogeneous catalyst with optimum reaction conditions to hydroprocess bio-oil to transportation fuels.

1.6   Objectives

The main objective of this study was to upgrade the biomass derived fast pyrolysis bio-oil into hydrocarbons via HDO. In the first-stage HT conditions are applied to raw bio-oil to produce partially upgraded and organic liquid product with properties similar to boiler fuel. In the second-stage HC, organic liquid product from the HT process is further hydrocracked with application of severe or harsh temperature and pressure conditions to produce a hydrocarbon mix with properties suitable for direct blending with petroleum fuels. Subtasks are to:

1   Screen various catalysts to determine promising catalysts for both the HT and HC stages with respect to highest product yields and a low hydrocarbon oxygen content.

2.   Catalyze bio-oil at various reaction temperatures and times over a range of reactor pressures to select an optimal catalytic regime for both the HT and HC stages.

3.   Physically and chemically analyze the bio-oils and hydrocarbons produced to gauge the effect of the hydroprocessing treatments. Determine the energy efficiency and hydrogen consumption for both the HT and HC stages.

4.   Perform simulated and physical distillations of the hydrocarbon mixes produced by the hydroprocessing experiments. Compare hydroprocessed bio-oil product properties to those of petroleum diesel, gasoline and jet fuel.

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CHAPTER II

PRODUCTION OF STABILIZED BIO-OIL BY MILD HYDROTREATMENT OF
FAST PYROLYSIS BIO-OIL

2.1 Introduction

Over the next thirty years, e U.S. energy consumption in the transportation sector
is estimated to increase to over 30 quadrillion Btu (quads), according to the latest 2010
annual energy outlook report released from Energy Information Administration (EIA)
[1]. Typical U.S. transportation sector consumption fluctuated between 20 to 30 quads
from 1980-2008 periods. Based on the rate experienced over this period petroleum
consumption is estimated to increase to approximately 40 quads by the year 2035 [1].
Replacement of a percentage of petroleum-derived fuels with bio-fuels will both reduce
greenhouse gas emissions and increase fuel supply as we approach peak petroleum oil
production. The U.S. Department of Energy (DOE) and the U.S. Department of
Agriculture (USDA) recently published a report that conceives of replacing 30% of
current petroleum consumption with biofuels by the year 2030 [2].

Bio-fuels emit negligible amounts of sulfur, nitrogen and ash upon combustion.
Bio-oils produced by fast pyrolysis share these benefits with other biofuels and are a
recognized potential source of liquid transportation fuels [3-8]. Bio-oils are complex
oxygenated compounds being comprised of highly oxygenated chemicals such as esters,
carboxylic acids, ethers, ketones, aldehydes, phenolic derivatives and aliphatic and
aromatic alcohols [7, 10]. The presence of a high percentage of these chemical

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oxygenates is the main reason for bio-oil negative properties such as low volatility, low heating value, corrosiveness, immiscibility with fossil fuels, tendency to polymerize during storage and transportation [11, 10].

Raw bio-oil has been test combusted in diesel engines, both neat and as an emulsion containing diesel fuel. Raw bio-oil has also been tested in turbines and Stirling engines for the production of electricity. With the exception of the Stirling engine test researchers detected engine corrosion, deposits or wear and tear [8]. It is currently universally agreed that bio-oils must be upgraded prior to their utilization as engine fuels [10, 12, 13]. The chemical and physical properties of bio-oils can be improved by partial or total deoxygenation of the oxygenated compounds present in high proportion in the bio-oil. When achieved by replacement of oxygen atoms by hydrogen atoms this process is known as hydrodeoxygenation (HDO) [6, 7, 11, 12, 14, 15]. HDO is similar to the hydrodesulfurization (HDS) process used in petroleum refineries for removing the sulfur from crude oil.

Catalyst selection is highly important for successful HDO treatment. The majority of HDO catalysts are traditional hydrotreating catalysts used for petroleum crude HDS. The most frequently used HDS catalysts are sulfided CoMo, NiMo and precious metal catalysts [16-19]. Researchers have demonstrated significant deoxygenation of bio-oil from application of heterogeneous sulfide catalysts [12]. However, these catalysts require presulfidation to maximize their catalytic activity. Presulfidation is appropriate for preparation of an HDS catalyst because sulfur is present in the treated petroleum crude. But bio-oil is a sulfur free liquid and addition of external sulfur will transfer the sulfur to the resulting hydrocarbon fuel which is environmentally disadvantageous as well as increasing catalyst cost. Noble metals are known to be effective hydrotreating catalysts

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without need of presulfiding, but their usage will increase the cost of catalysis. There exists a need for a highly active hydrotreating catalyst that does not require presulfidation and which is not a costly precious metal catalyst.

Previous studies on upgrading of bio-oil demonstrated that bio-oil could be converted to gasoline weight hydrocarbons with reasonable hydrogen consumption using a two-stage process of mild hydrotreating (HT) in the first-stage and application of more severe temperature and pressure conditions in a second-stage hydrocracking step (HC). HT of bio-oil produces a stabilized bio-oil with improved properties such as reduced oxygenates (aldehydes, acids, esters and phenolic derivatives) thereby reducing the polymerization of the bio-oil and decreasing the viscosity of the mixture. HT process is expected to remove oxygenates to a significant extent (~60 wt%). Subsequently HC reduces the oxygen content (~100 wt%) and produces fuel with properties acceptable for direct blending with petroleum fuels.

The objective of this portion of the study was to screen catalysts to determine the most effective catalyst by performing HT experiments in a stirred high-pressure autoclave and to determine the characteristics, relative to petroleum fuels, of the HT organic liquid.

Following selection of an effective batch reactor catalyst, the reaction temperature and reaction time were optimized. Regeneration studies were performed to determine the longevity of the most effective catalyst. Aging studies were performed to compare the characteristics of HT organic liquid to raw bio-oil. Physical and chemical analysis of the HDO bio-oil properties were determined and compared to those of petroleum fuels.

2.2   Materials and methods

2.2.1   Bio-oil production via fast pyrolysis of biomass

A 3-7 kg/hr augur-feed pyrolysis reactor developed by Department of Forest

Products, Mississippi State University (MSU) produced the required bio-oils for all the

experiments. The reactor was operated at a temperature between 400 and 550 ^{o}C. Bio-oils

were produced from loblolly pine. The feedstock was produced by chipping the loblolly

pine into particles of 1 to 3 mm diameter followed by drying to approximately 10%

moisture content prior to pyrolysis. The oil was filtered after preparation and stored at -10

^{o}C to avoid aging resulting from polymerization of the bio-oil. The MSU auger reactor

has been extensively tested with respect to operating conditions for pine feedstocks. As

shown in Table 2.1 bio-oil yield was approximately 65 wt% dry weight basis; byproducts

were 12 wt% char and 23 wt% non-condensable gases as shown in Table 2.1.

Table 2.1   Typical yields from the fast pyrolysis of pine feedstock produced by the
MSU auger reactor.

Products	wt%.
Bio-oil	65
Char	12
Non-condensable gases[a]	23

[a] by difference

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Figure 2.1   Production of bio-oil by auger reactor technology at MSU; wood particle in feed shown.

Table 2.2 summarizes the characteristics of the raw bio-oil prior application of the HT process. The initial raw bio-oil had an acid value of 94; water content was 23.5 wt%; pH was 2.5; density was 1.15 g/mL; viscosity was 7.15 cSt at 40 ^{o}C; bio-oil ash content was 0.1 wt%; HHV was 17 MJ/kg; lower heating value (LHV) was 15.6 MJ/kg; flash point ranged from 40-65°C; carbon content was 52 wt%; hydrogen content was 6.4 wt%; nitrogen content was 0.2 wt%; oxygen content was 43.5 wt%; and sulfur contained in the bio-oil was less than 0.01 wt%.

Table 2.2   Physical and chemical properties of raw bio-oil produced from pine feedstock by MSU auger reactor.

Property	Value
acid value (mg KOH/g)	94
water content (wt%)	23.5
pH	2.3
density (g/mL)	1.15
viscosity (cSt) at 40 ^{o}C	7.15
higher heating value (HHV),MJ/kg	17.0
lower heating value (LHV), MJ/kg	15.6
ash content (wt%)	~0.1
flash point (^{o}C)	40-65
elemental composition (wt%)	
C	~52
H	~6.4
O^{a}	~43.5
N	~0.2
S	<0.01

[a] by difference

2.2.2   Catalysts

Six commercial catalysts and one proprietary catalyst were selected for screening studies; the catalysts are listed in Table 2.3 with their supplier name and active metal content defined for those catalysts for which this information was available. The selected catalysts included four noble metal catalysts such as ruthenium on carbon (Ru/C), palladium on carbon (Pd/C), platinum on carbon (Pt/C) and platinum on alumina (Pt/Al2O3). These were obtained as powders from Sigma-Aldrich and contained 5 wt% of active metal. Three traditional hydrotreating catalysts were selected: nickel

molybdenum on gamma alumina (NiMo/Al) obtained from Sud-Chemie, cobalt
molybdenum on gamma alumina (CoMo/Al) obtained from Alfa-Aesar and a proprietary
MSU-1 catalyst with proprietary heterogeneous catalyst on a proprietary catalyst support
was obtained from an undisclosed vendor.

Table 2.3   Properties of catalysts used in this catalyst screening study.

Catalyst	Vendor	Active metal, wt%
Ru/C	Sigma-Aldrich	5
Pd/C	Sigma-Aldrich	5
Pt/C	Sigma-Aldrich	5
Pt/Al$_2$O$_3$	Sigma-Aldrich	5
NiMo/Al	Sud-Chemie	proprietary
CoMo/Al	Alfa-Aesar	proprietary
MSU-1	Undisclosed vendor	proprietary

2.2.3   Chemicals and gases

Acetone, methanol and hexane were obtained from Sigma-Aldrich and
dimethylsulfoxide (DMSO) solution was obtained from Gaylord Chemicals. Ultra high
purity hydrogen (>99.99%) and helium (>99.99%) gases were supplied by Nex-Air.

2.2.4   Hydrodeoxygenation experiment

Bio-oil was mildly hydrotreated in a 450 mL high-pressure batch autoclave (Parr
Instruments Co.). A schematic of the autoclave processing system is given in Figure 2.2.
The maximum pressure and temperature achievable by the autoclave is 5000 psig and
500 $^\circ$C, respectively. The autoclave is equipped with an electrical heating/cooling system

control of the autoclave temperature. Two input gas valves are available to allow input of 2 gas types simultaneously, if desired. Reaction exit gas is expelled by a valving system.
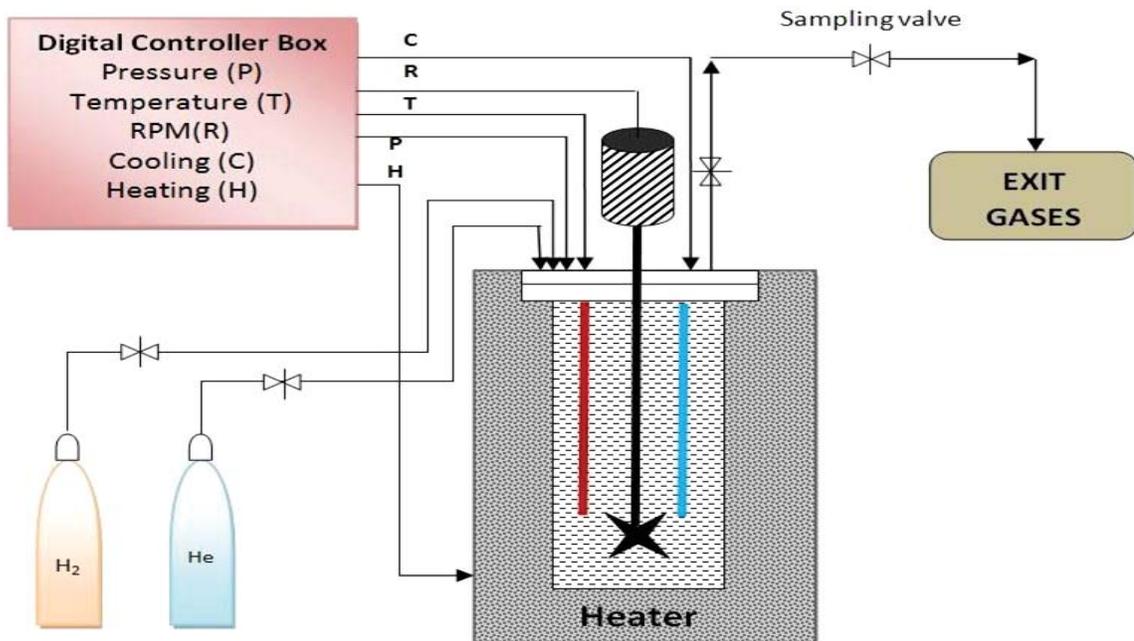
Figure 2.2   Schematic representation of the high-pressure batch autoclave that performed the bio-oil hydroprocessing experiments.

2.2.5   HT experimental procedure

The reactor was filled with bio-oil (100 g) and catalyst (5 wt% on basis of pyrolysis oil). Subsequently, the reactor was flushed three times with helium gas and pressurized with a pre-determined value (1500 psig) of hydrogen gas at room temperature. The reactor was heated to the intended reaction temperature (350 ^{o}C) with a heating rate of 10 ^{o}C/min and kept at that temperature for the intended reaction time (2-4 h). The reactor contents were stirred at 1000 rpm with a magnetically driven stirrer with speed controlled digitally.

The autoclave pressure developed during hydrotreating was recorded at 15 min intervals for each temperature tested. The final autoclave pressure was recorded for the

mass balance calculation and the gas phase was sampled with a 1-liter SKC gas sampling bag. Following each 2-4 h reaction, the reactor was cooled to ambient temperature and the liquid product of the autoclave was collected.

Following hydrotreatment the liquid product consisted of two phases: an organic phase and a water phase. These liquid products were centrifuged with a Fisher Accuspin-3R at 4000 rpm for 2 h at 10 $^{\circ}$C to obtain a clean separation of the organic and water phases. Following centrifugation the organic phase floated on the water phase allowing siphoning of the water by Buckner funnel.

Following the reaction and removal of the product from the reactor residual solids were present on the reactor walls. Also, a small amount of char was present at the bottom of the two-phase liquid fraction removed from the reactor. This char was maintained in the centrifuge tube when the organic and liquid phases were poured into the Buckner funnel. The solids cleaned from the reactor walls and the solids collected from the bottom of the centrifuge tube were both combined and subsequently washed with acetone and oven dried at 100 $^{\circ}$C overnight. The separated char, organic fraction and aqueous fraction were weighed to determine the total weight of product resulting from the hydrotreatment.

The catalytic HT reactions were conducted at 350 $^{\circ}$C and 1500 psig for 4 h reaction time. The hydrotreatment reaction time was selected from earlier research performed by Wildschut et al. [23, 25, 27]. To eliminate mass transfer effects, CoMo/Al, NiMo/Al and Pt/Al catalyst pellets were crushed into a fine powder prior to their usage. Presulfiding of CoMo/Al and NiMo/Al catalysts were carried out by mixing the catalysts with 2 wt% of DMSO at 240 $^{\circ}$C for 3 h in 1000 psig of H_2 pressure.

2.2.6   Optimization of temperature and reaction time for MSU-1 Catalyst

The HT process for the MSU-1 catalyst was further optimized to obtain higher

organic liquid yields with lower oxygen content with respect to reaction temperature and

time applying the variables as shown in Table 2.4. Reaction time applied was 4 h; H2

pressure was 1500 psig; applied temperatures ranged between 200-400 ^{o}C at 50 ^{o}C

intervals. To determine the influence of reaction time reaction times between 1 and 3 h at

1 h intervals were tested, applied H_2 pressure was 1500 psig and temperature was 350 ^{o}C;

for each autoclave experiment the bio-oil quantity utilized was 100 g and catalyst weight

was 5 g.

Table 2.4   Variables applied during the optimization of temperature and reaction time
for MSU-1 catalyst.

Variables	Effect of Temperature	Effect of reaction time
Time, h	4	1, 2, 3 and 4
Pressure, psig	1500	1500
Temperature, ^{o}C	200, 250, 300, 350 and 400	350
Bio-oil, g	100	100
Catalyst, g	5	5

2.2.7   Catalyst regeneration procedure

Catalyst regeneration studies were also performed to provide insight into catalyst

activity in terms of product yields and deoxygenation efficacy over time by using the

same catalyst for multiple runs. The catalyst regeneration experiments were also

performed with 100 g of bio-oil; 5 g of catalyst; at a temperature of 350 ^{o}C for 1 h under

1500 psig H_2 pressure. Following application of each HT autoclave run, the spent catalyst

was collected and washed with acetone and oven dried overnight at 110 ^{o}C. Subsequently

the catalyst was calcinated at 500 ^{o}C for 4 h to remove any coke/char on the catalyst. This was followed by the addition of a 2.5 wt% of new catalyst to restore the total catalyst weight to 5 wt%. The spent catalyst was regenerated four times following the procedure described above for the HT of bio-oil.

2.3   Analysis of raw and upgraded bio-oils

2.3.1   Physical properties

Raw bio-oil and HT organic liquid densities were determined by Anton Parr DMA 35n portable density meter. Viscosities were determined by Ubbelohde capillary viscometer at 40 ^{o}C water bath temperature. Kinematic Viscosity was measured by multiplying flow time of the liquid with a calibration constant (0.02986) for the viscometer. Flash point was tested by Koehler flash point tester Model No. K16200. HHV was determined by Ika-5000 bomb calorimeter.

The acid value was determined by dissolving 1 g of bio-oil in 50:50 isopropanol/water mixtures and titrating to a pH of 8.5 with 0.1N KOH solution. The acid values were calculated as the number of milligrams of KOH equivalent to 1 g of sample. The pH values were determined by adding 1 g of bio-oil to 50 mL of water, stirring, and measuring the pH with an Orion Model EA920 pH meter. Elemental carbon, hydrogen, and nitrogen were determined by EAI CE-440 elemental analyzer with oxygen content determined by difference. Water content of the bio-oil was determined by the Karl-Fisher titration by standard methods [19, 20].

2.3.2   Chemical analysis

The gas chromatography coupled with mass spectrometry (GC/MS) analysis of the raw bio-oil were performed with a Hewlett-Packard HP 5890-Series II GC equipped

with a Hewlett-Packard HP 5971 series MS. The calibration method for determining bio-oil chemical components was described in a previous paper reported by Ingram et al. [9]. Briefly, a representative sample (0.2 g) of each specimen was weighed to the nearest 0.1 mg and diluted to 10 mL with methanol. One milliliter of this solution was transferred to an auto-sampler vial and spiked with 10 mL of a 4000 µg/mL (ppm) internal standard just prior to analysis. A dilute sample of 1 µl was injected onto ZB-5 capillary column of (30 ml x 0.32 mm ID x 0.25 µm film thickness). The initial oven temperature of the GC was 40 °C for 4 min and the temperature was then programmed at a rate of 5 °C/min to 270 °C. The injector and detector temperatures were 270 and 250 °C, respectively, and the carrier gas was He of 99.99% purity. The m/z (ratio of mass to charge) values, which represent the fragment ions of the compounds, were recorded for each compound.

FTIR spectroscopy is proven to be a very versatile technique for identification of organic functional groups in the bio-oil and HDO product oil. Fourier transform infrared (FTIR) spectra were obtained by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed by Varian-Resolutions software. NMR has proven to be a versatile technique for the identification of organic molecules, even in complex mixtures. NMR is concerned with magnetic properties of certain atomic nuclei, notably the nucleus of hydrogen atom- the proton and that of carbon-13 an isotope of carbon. Proton-nuclear magnetic resonance (^{1}H-NMR) appears to be a useful technique for bio-oil characterization [7]. ^{1}H-NMR spectra were recorded on a 300 MHz NMR (Bruker) instrument and spectral interpretation was performed by applying TOPSPIN 2.1.6 version software. All ^{1}H-NMR specimens were dissolved in a solution of $CDCl_3$ except water phases obtained from HT experiments which were dissolved in D_2O.

A Varian CP-4900 Micro Gas Chromatograph (GC) analyzed the gas composition of the remaining gas stream after each batch experiment. The Varian CP-4900 employs 4 independent GC channels. Channel.1, which has a 10 meter MS5A GC column and was utilized to analyze hydrogen, oxygen, nitrogen, methane, and carbon monoxide concentrations. Channel 2, which is equipped with a 10 meter PPQ GC column, was utilized to test the concentration of carbon dioxide and ethane. The Micro GC gas analysis conditions for this study are given in Table 2.5.

Table 2.5   Micro GC conditions for gas phase analysis of gases collected after the HT batch runs.

Channel No.	Injector Temperature (^{o}C)	Column Pressure (psig)	Column Temperature (^{o}C)	Sample Time (s)	Injection Time (ms)
No. 1	50	20	80	60	40
No. 2	110	20	60	60	40

2.4   Results and discussion

2.4.1   Catalyst screening studies

All HT experiments performed at 350 ^{o}C and 1500 psig of H_2 for 4 h reaction time resulted in the formation of a two-phase liquid comprised of immiscible organic and aqueous phases. For two of the catalysts, Pt/Al and CoMo/Al the organic fractions were heavier than the aqueous fraction; for the remaining five catalysts the organic fraction was lighter than water and, as a result, floated on the aqueous fraction. In addition to high density the heavy organic fractions had very high viscosity. For the purposes of this study I will refer to the organic fraction that was heavier than water as heavy oil; the organic fraction lighter than water will be termed light oil. Previous researchers have noted the

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production of heavy oils of the type described and have attributed their production to incomplete hydrotreating [19, 32]. In all cases the aqueous phases produced had very high 88% water content and contained minor amounts of dissolved organic compounds.

Experimental results are shown in Figure 2.3. Five catalysts produced light oil organic fractions ranging from 32 to 38 wt%. Highest oil yield was obtained for MSU-1 (38 wt%) and lowest yields were for Ru/C (32 wt%). The high yields provided by MSU-1 catalyst were considered to be due its dual functional nature, exhibiting both acidic and hydrogenation activity. The low yield obtained for Ru/C was likely due to its high activity in converting oxygenated compounds to gaseous, rather than liquid, components. Support for this observation is provided by the Figure 2.4 gas yield data showing that the highest gas phase (18.89 wt%) yields were obtained for Ru/C catalyst.

CoMo/Al and Pt/Al catalysts both gave approximately 36 wt% organic fraction yields and these were heavy oils. The remaining five catalysts produced light oil organic fraction yields ranging from approximately 32 to 38 wt%. The highest yielding catalyst was MSU-1 with 37.9 wt% yield.

The aqueous fraction formed by the catalytic hydrotreating reactions ranged from 35-46 wt% of the total products formed. Pt/Al catalyst produced the lowest amount of water at 34.8 wt%. This catalyst also produced heavy oil, believed to result from lower hydrotreatment of the bio-oil. Therefore, it appears that reduced conversion of oxygenated compounds resulted in lower water production. Amount of char formed ranged from 6.5 to 11.1 wt%. By contrast, CoMo/Al also produced heavy oil but also produced considerably higher water yield at 42.2 wt%. There is no obvious explanation as to why CoMo/Al did not HT the heavy oil fully but also produced a considerable amount of water.
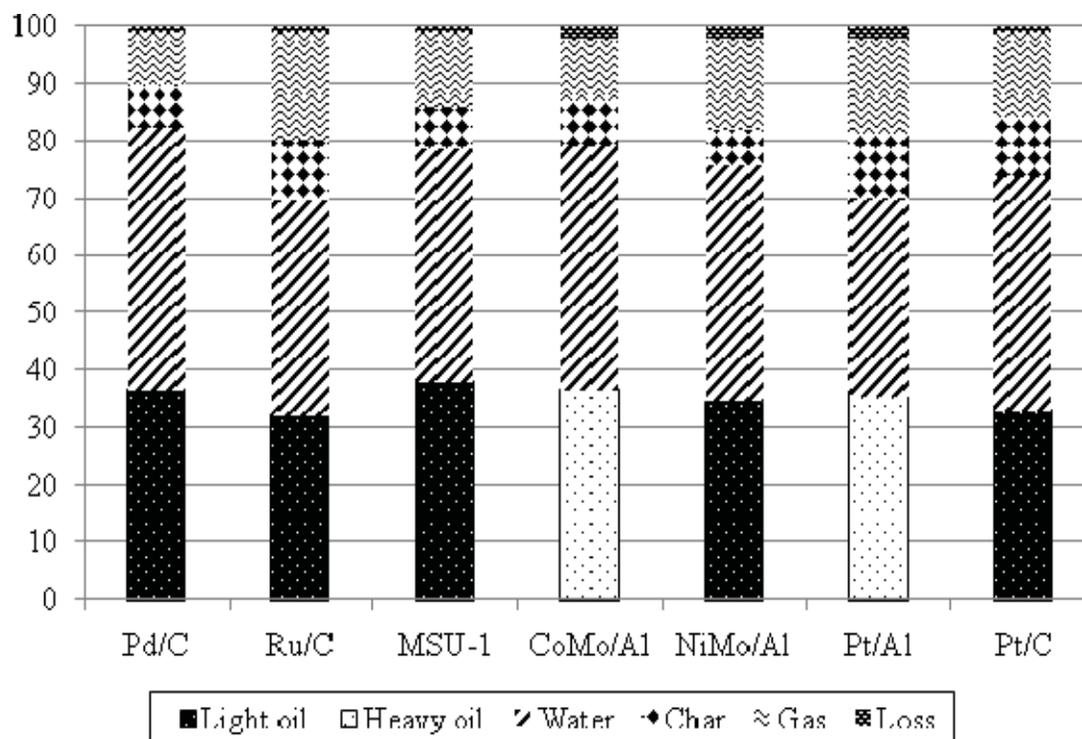
Figure 2.3   Mass balances for HT of bio-oil with screened catalysts (350 ^{o}C, 1500 psig, and 4 h).

Char yields ranged from approximately 6.4 to 11 wt%. The highest char yields were for Pt/Al at 11.1 wt% and 10.8 wt% for Ru/C. The high char yield for these catalysts is considered to be due to their high selectivity and reactivity towards furanic and carbohydrate compounds to form solids. This interpretation is also supported by the high gas yields of 18.9 wt% and 16.6 wt%, respectively, for Ru/C and Pt/Al. Therefore, the high reactivity of these two catalysts converted furans and carbohydrate compounds to both char and gas. Mass balance HT results for each catalyst are given in Appendix A (Table A.1).

In addition to the formation of two liquid phases, significant amounts of gas were also formed during the HT experiments. Gas composition was calculated by difference of liquid phases and solid yields. The amount of gases formed varied between 13 and 20

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wt%. The gas phase composition after reaction was analyzed and the results are presented

in Figure 2.4. The lowest gas yields were obtained for Pd/C and highest gas yields were

obtained for Ru/C. The most likely the reason for the high gases for Ru/C is due to its

high activity towards conversion of oxygenated compounds into gases rather than liquids.
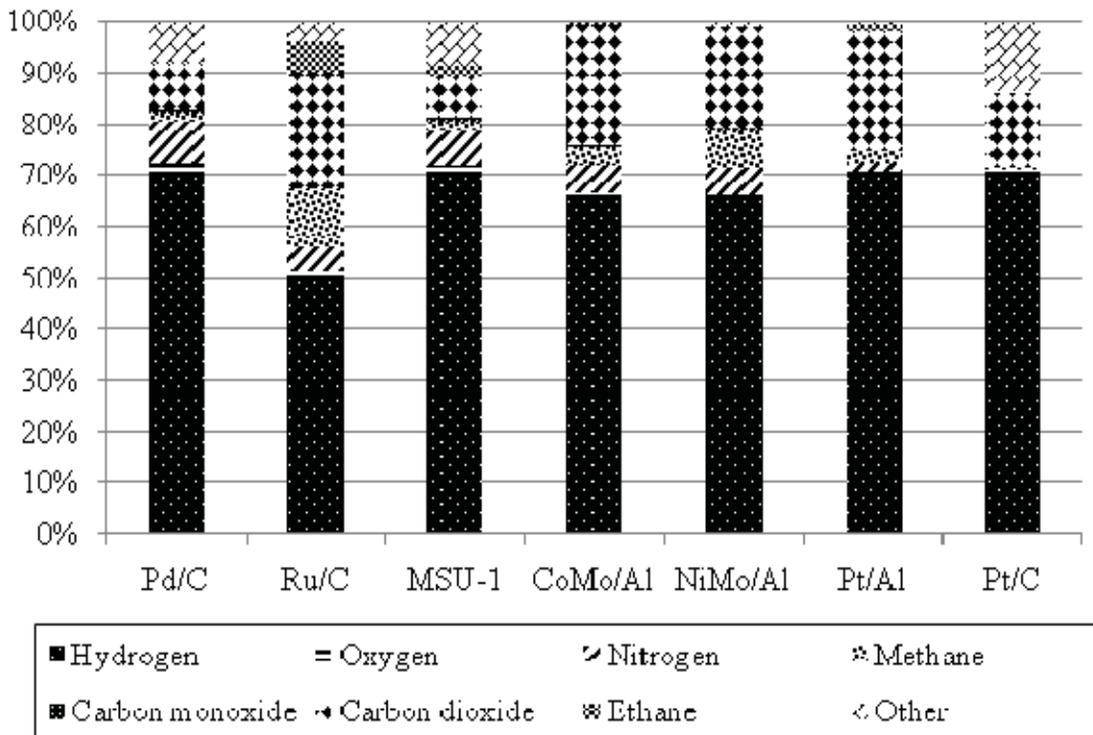
Figure 2.4   Gas phase analysis of HT of bio-oil (350 $^{\circ}$C, 1500 psig, and 4 h) using
               various catalysts.

The main gas phase component produced by the HT reaction was unreacted

hydrogen. CO_2 was the second the major component of the HT gases produced. A

possible pathway for the formation of CO_2 is decarboxylation of organic acids and esters

present in bio-oil. Typical bio-oil contains organic acids (acetic, formic and oleic) in the

range between 10 and 20 wt% [10]. CH_4 was also observed in a few samples with the

highest production for by Ru/C catalyst.
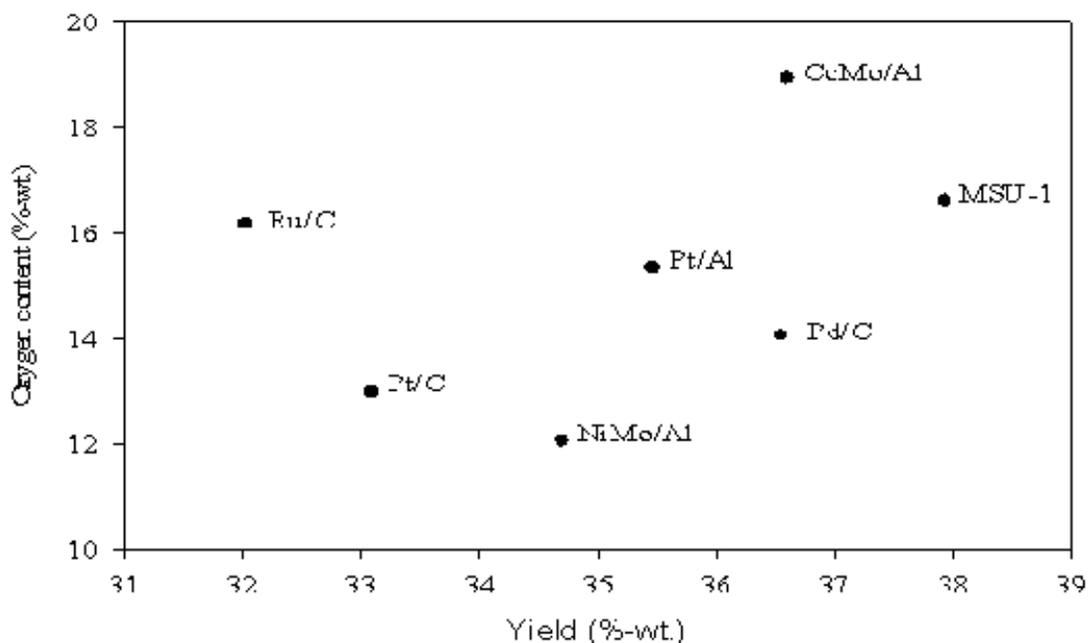
Figure 2.5   Oxygen content of organic fractions plotted versus oil yields by catalyst type for the bio-oil HT experiments performed at 350 ^{o}C under 1500 psig H_2 for 4 h.

The heavy and light oil yields and their respective oxygen contents are a good measure of the efficacy of catalyst performance. Figure 2.5 shows oxygen content on y-axis as a function of yield on the x-axis for each catalyst tested. The organic conversion products of both Pt/Al and CoMo are identified as heavy oils with the products of the remaining catalysts identified as light oils. The total organic product yields for all seven catalysts varied between 32 and 38 wt%. The highest oil yields were obtained for MSU-1 and Pd/C and lowest for Ru/C. The low yields for Ru/C is in accord with the previous observation that the high activity of Ru/C results in high gas yield at the cost of conversion to liquid product.

The oxygen content of the organic liquid product for all seven catalysts varied between 12 and 19 wt%. Highest oxygen content was observed for CoMo/Al while the lowest was for NiMo/Al. It is not surprising that CoMo/Al had high oxygen content. As

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previously noted CoMo/Al produces a heavy oil that is not fully hydrotreated and would therefore, be expected to contain unreacted oxygenates. In addition, CoMo/Al also results in production of considerable water (Fig. 2.4) which, of course, is comprised of a large amount of oxygen. NiMo/Al, by contrast to CoMo/Al, produced relatively less water (Fig. 2.3) and produced a light organic liquid that is, apparently, more fully hydrotreated than that produced by other catalysts.

Van-Krevelen plots of molar H/C vs O/C are the best method for the evaluation of quality of the product oils and hydrogenation activity of the screened catalyst [17]. Molar H/C vs O/C ratios for raw bio-oil compared to those for the organic products produced by the seven catalysts are shown in Figure 2.6. Higher hydrogenation corresponds to a higher molar H/C ratio and a lower molar O/C ratio [17]. Figure 2.6 clearly shows that raw bio-oil has low molar H/C and high molar O/C ratios due to the presence of water and high proportion of oxygenated compounds. Because the catalyzed organic products have approximately the same O/C ratio the quality of hydrotreament can be determined by comparison of the H/C magnitudes.
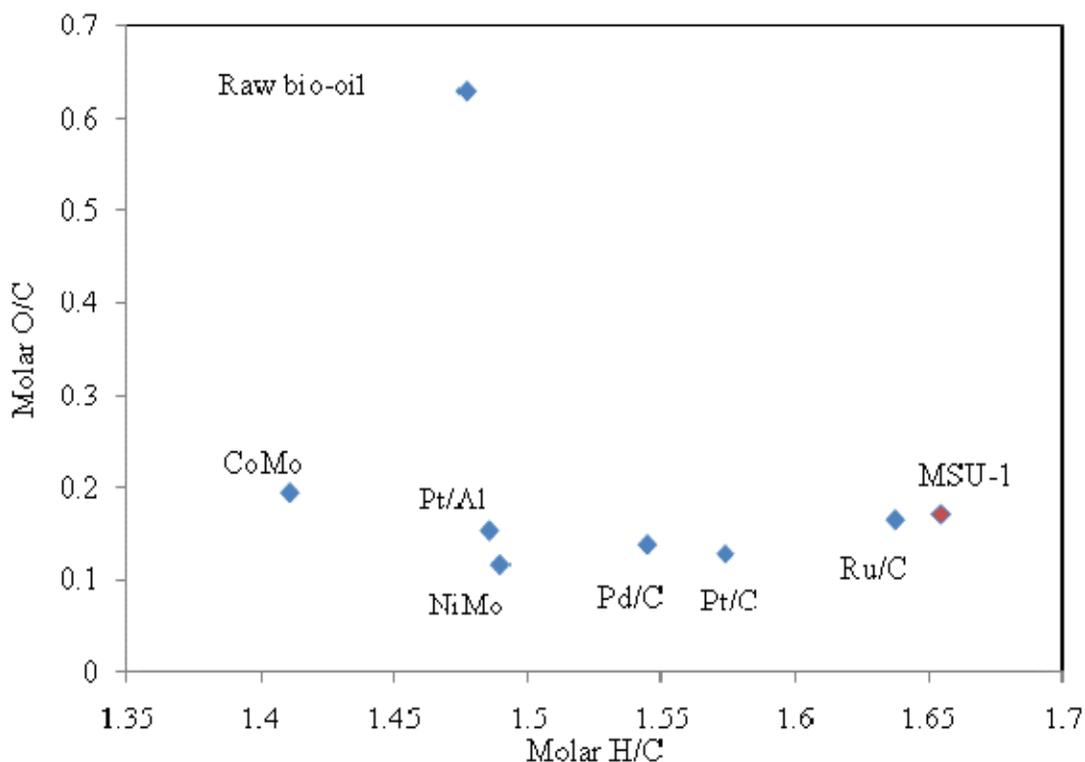
Figure 2.6   Van Krevelen plots of molar H/C-O/C ratios for each product oil produced by each catalyst during the HT experiments.

An analysis of variance (ANOVA) was performed on the H/C results of the organic products by catalyst type. The ANOVA was highly significant at the 0.001 level allowing comparison of means by Fisher's protected LSD method. Figure 2.7 provides a graph comparing the H/C ratio values and results of comparison of means tests for each organic product by catalyst. As shown in Figure 2.7 MSU-1 and Ru/C had the highest H/C ratio with respective values of 1.67 and 1.62 but did not differ significantly among themselves. Pd/C, Pt/C and NiMo/Al had significantly lower respective H/C ratios of 1.54, 1.53 and 1.49 and did not differ among themselves. NiMo/Al did not differ significantly from Pt/Al that had a H/C ratio of 1.45. Likewise, CoMo/Al whose H/C ratio was 1.41 did not differ significantly from Pt/Al. These results clearly show that by the H/C ratio criterion the MSU-1 and Ru/C produce superior organic products.
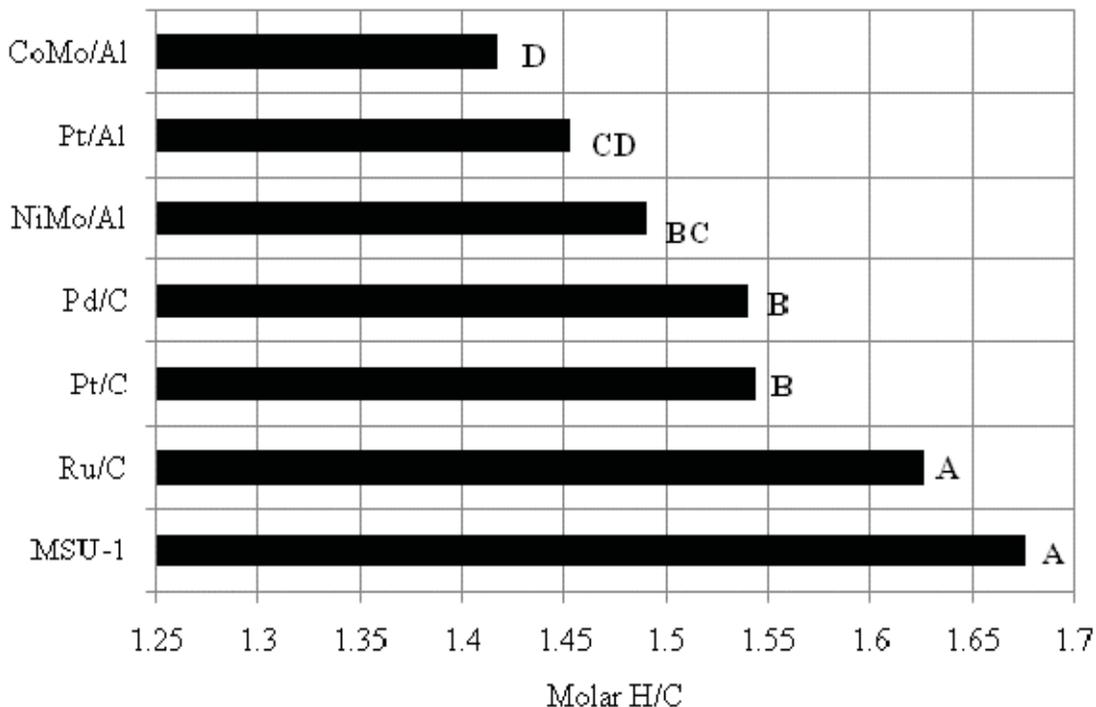
Figure 2.7   Comparison of means test results comparing organic oxygen content of liquid product values by catalyst type. Different letters following histograms indicate significant difference at the 0.05 level.

An ANOVA was performed on the yield values for the organic catalysis products. The ANOVA was highly significant with a p-value of 0.0001 allowing performance of comparison of means. Results of the comparison of means tests are given in Figure 2.7. These results show that MSU-1 had the significantly highest yield at 38.0. Pd/C, CoMo/Al and Pt/Al had significantly lower respective yields of 36.1, 35.9 and 35.4 wt%. Significantly lowest yields Fwere for NiMo/Al, Pt/C and Ru/C with respective yields of 34.5, 33.1 and 32.5 wt%. The statistical analysis of yield results shows that MSU-1 produced significantly higher yields than the 6 other tested catalysts.
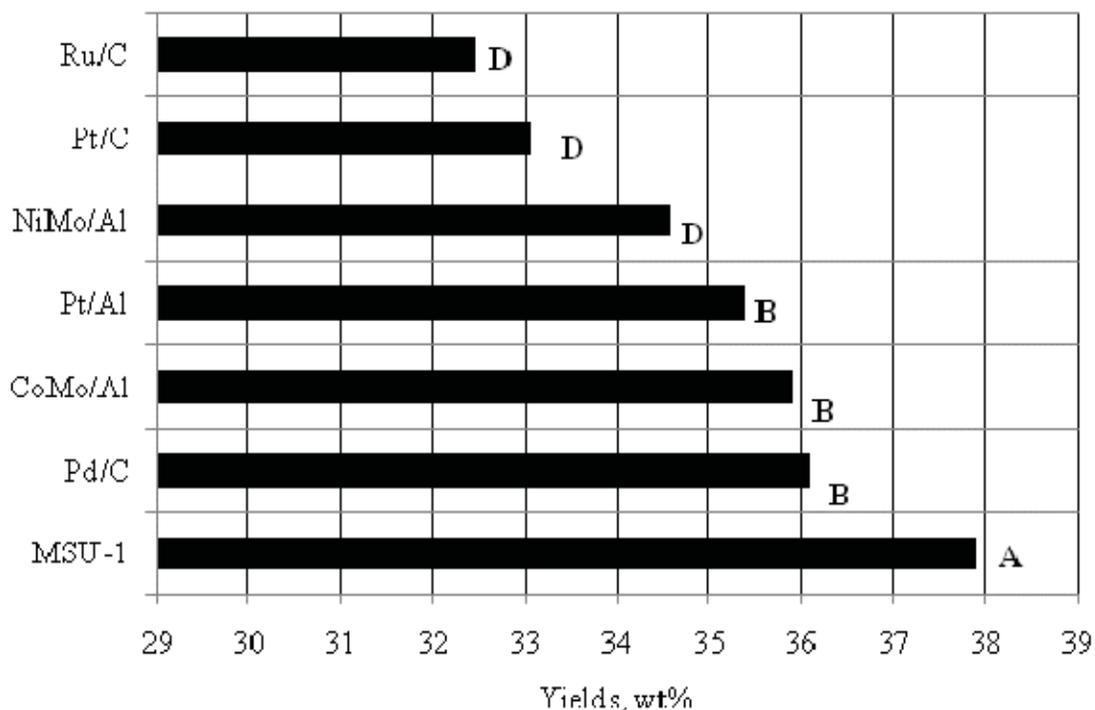
Figure 2.8   Comparison means test results for organic liquid product yields by catalyst type. Different letters following histograms indicate significant difference at the 0.05 level.

The results of the statistical analysis of both H/C ratio and yield indicate that the MSU-1 catalyst had significantly higher results in terms of both. Ru/C had an HC ration equal to that of MSU-1 vur but in terms of yield it ranked significantly the lowest. Similarly, Pt/C and Pd/C ranked significantly lower than MSU-1 and Ru/C in terms of H/C ratio. However, Pt/C had a yield that was significantly lower than both MSU-1 and Pd/C and CoMo/Al which indicated that it was much less effective as a HT- catalyst compared to MSU-1. Pd/C by contrast ranked just below MSU-1 in terms of yield but was only moderately effective in terms of H/C ratio. The result of the combined comparisons of H/C ratio and yield clearly indicate that MSU-1 catalyst is a better hydrotreating catalyst compared to other tested catalysts. Results for the remaining

catalysts in terms of both H/C ratio and yield are mixed with some having relatively high H/C values but lower yields.

Table 2.6 gives some important chemical and physical properties of the organic products obtained for each catalyst tested. The acid value of the organic liquids produced by catalysis ranged between 47 and 52 mg KOH/g. These values are all approximately one half of the value of raw bio-oil with an acid value of 95. Organic product acidity was also measured in terms of pH with pH values ranging between 3.3 to 4.5. Water content values of the organic products ranged between 2.5 to 6 wt%; HHV between 33 to 37 MJ/kg; and density between 0.95 to 1.03g/mL.

Based on the results of organic product yields and oxygen content we have determined that the MSU-1 catalyst had the significantly highest yield and lowest oxygen content. In terms of the remaining physical and chemical test results we find that the MSU-1 catalyst had the lowest water content, highest HHV and lowest density. These are all positive attributes regarding the potential for a liquid biocrude to be refined in current petroleum refineries. In terms of the remaining chemical and physical properties the MSU-1 catalyst had an acid value that was higher than four other organic products but lower than for two others. Therefore, magnitude of acid value was not a deciding factor regarding selection of MSU-1 as the best hydrotreating catalyst. In terms of pH the MSU-1 catalyst is the second highest. Therefore, the MSU-1 catalyst is the best catalyst in terms of yield, oxygen content, water content, HHV and density. It had a pH just below that of the catalyst that produced the highest pH. The acid and pH values of the MSU-1 catalyst do not exclude it as the best performing catalyst by the most important measures.

The comparison of the properties of the organic liquid products produced from the HT experiments for the seven catalysts tested have resulted in identification of MSU-1 as

the best performing catalyst. For that reason MSU-1 was selected as the catalyst for

which to determine the optimum reaction time and temperature to produce highest yield

and best properties of the organic product.

Table 2.6   Comparison of physical and chemical properties of the organic products obtained for each catalyst tested with the raw bio-oil.

Property	Raw Bio-oil	Pd/C	Ru/C	MSU-1	CoMo	NiMo	Pt/Al	Pt/C
Acid value, mg KOH/g	95	48.50	52.16	52.00	51.30	59.67	47.17	51.37
Water, wt%	23.5	3.81	5.96	2.26	4.15	3.90	3.79	3.48
HHV, MJ/kg	17	33.01	35.55	36.23	35.97	37.04	35.10	35.32
pH	2.5	3.40	4.01	3.93	3.83	4.41	3.86	3.32
Density, g/mL	1.12	0.98	0.95	0.96	1.03	0.99	1.02	0.97

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2.4.2 Temperature optimization for hydrotreatmen of bio-oil with MSU-1 catalyst

Bio-oil was catalyzed with MSU-1 catalyst at various temperatures (200 to 400 $^{\circ}$C at 50 $^{\circ}$C intervals under 1500 psig of H_2 pressure determine an optimum temperature at which to perform the reaction. The results from the temperature optimization experiments are presented in Figure 2.9. The two highest temperatures of 350 and 450 $^{\circ}$C produced light oils while the lower temperatures of 200, 250 and 300 $^{\circ}$C produced only heavy oils. The overall product oil yields, whether of light or heavy organic product ranged from approximately 31 to 38 wt%. The light oils produced yields in the 31 to 38 wt% range for temperatures of 350 and 400 $^{\circ}$C. Heavy oil yields ranged from approximately 33 to 38 wt% yield for temperatures of 200, 250 and 300 $^{\circ}$C.
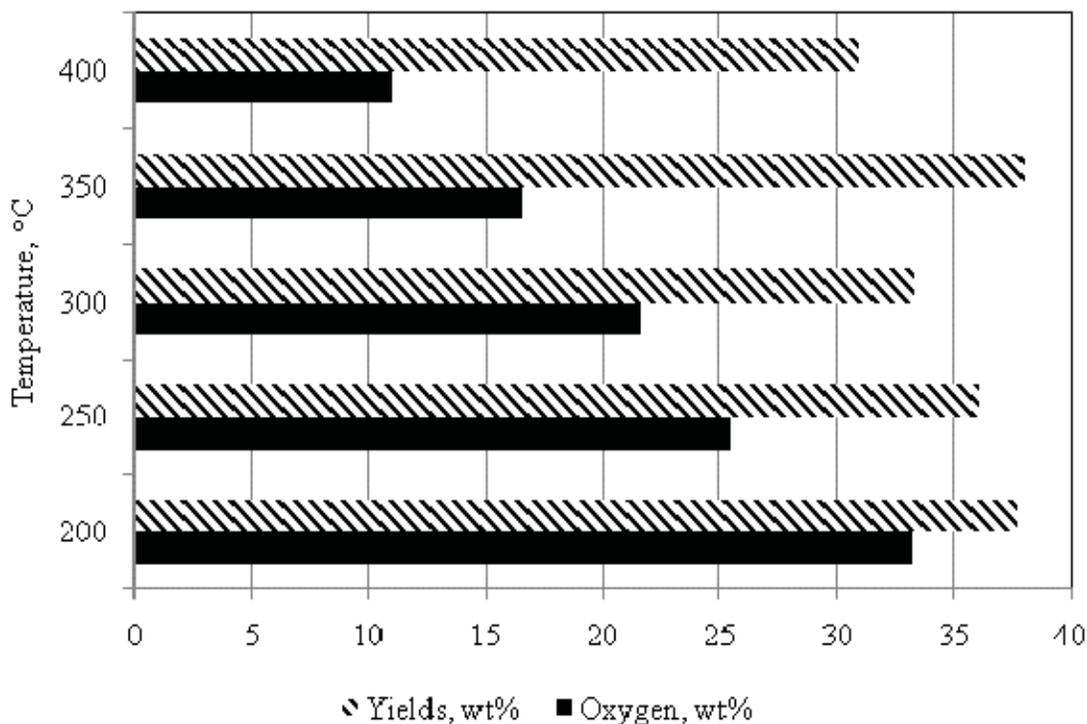
Figure 2.9   Effect of reaction temperature on the HT of bio-oil using MSU-1 catalyst.

Oxygen content values were directly correlated with applied temperature with highest oxygen content value of 33.3 wt% observed at the lowest applied temperature of 200 ^{o}C decreasing almost linearly to 11.0 wt% oxygen content for the highest 400 ^{o}C temperature. The oxygen content decrease from lowest to highest temperature was a nearly equal 21.7 wt% for each incremental 50 ^{o}C increase in temperature.

The optimum catalysis temperature, therefore, could be selected based on the highest light oil yield with reasonably low oxygen content. These conditions are satisfied by the 350 ^{o}C temperature at which a 39 wt% organic product yield was achieved with an oxygen content of 16.7 wt%. The 400 ^{o}C temperature, while producing the lowest oxygen content of 11.0 wt% had a relatively low light organic liquid yield of 31 wt% representing a 15 wt% loss in yield compared to that for the 350 ^{o}C temperature.

2.4.3 Effect of reaction time on mass balance from HT organic liquid with MSU-1 catalyst

Figure 2.10 shows the mass balances resulting from hydrotreatment of bio-oil with MSU-1 catalyst at 350 ^{o}C. The reaction times tested ranged from 1 to 3 h at 1 h intervals. The mass balances shown are given as aqueous fraction, organic liquid, solids and gases. Mass balances closures ranged between 95-99 wt%.
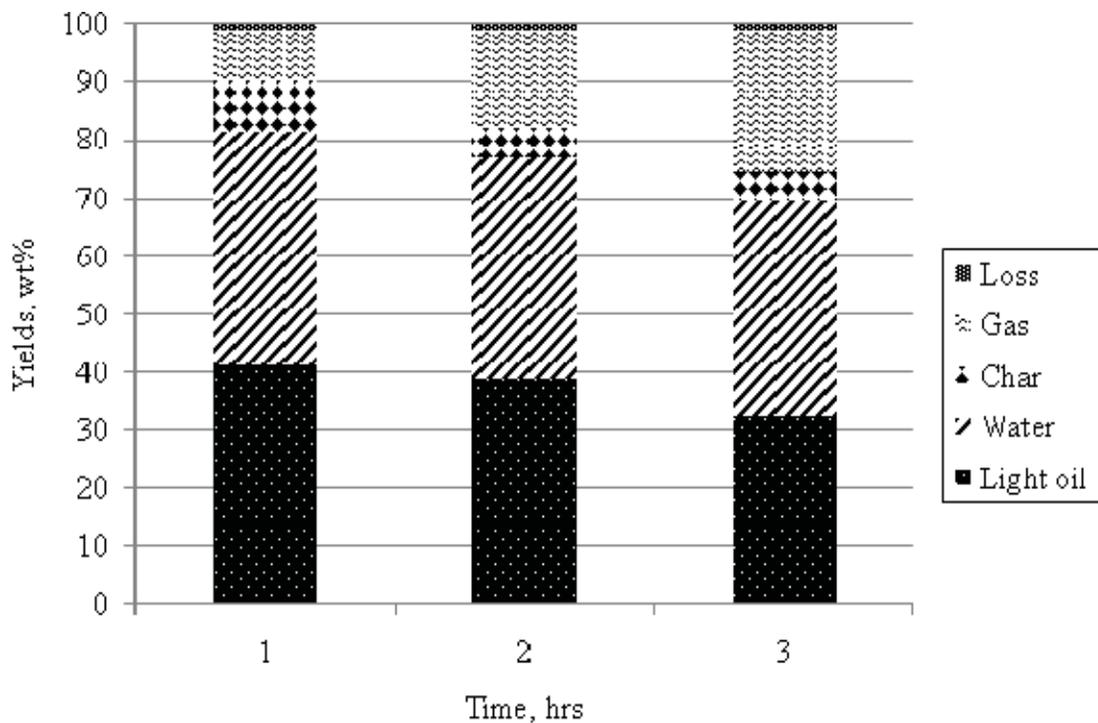
Figure 2.10   Mass balances resulting from HT of raw bio-oil at four temperatures with MSU-1 catalyst at a temperature of 350 ^{o}C and H$_2$ pressure of 1500 psig.

The overall product oil yields ranged from approximately 33 to 41wt% and the oxygen content of the organic liquids varied between 9 and 24 wt%. The organic liquid yields show a decreasing trend for the reaction times above 1 h. The liquid yield decline for the 2 and 3 h reaction times appear to be directly correlated to the increase in gas yields for those times as shown in Figure 2.11. This figure indicates that the liquid organic product was maximized after A 1 h reaction time and that this liquid product was converted to gas as the reaction time continued for an additional 2 h. Char yields also declined after the first hour of HT declining from 8.6 wt% at 1 h to 5.2 and 4.8 wt%, respectively, at 2 and 3h. It appears that the char was also converted to gas over the 2h of additional reaction time above 1 h.
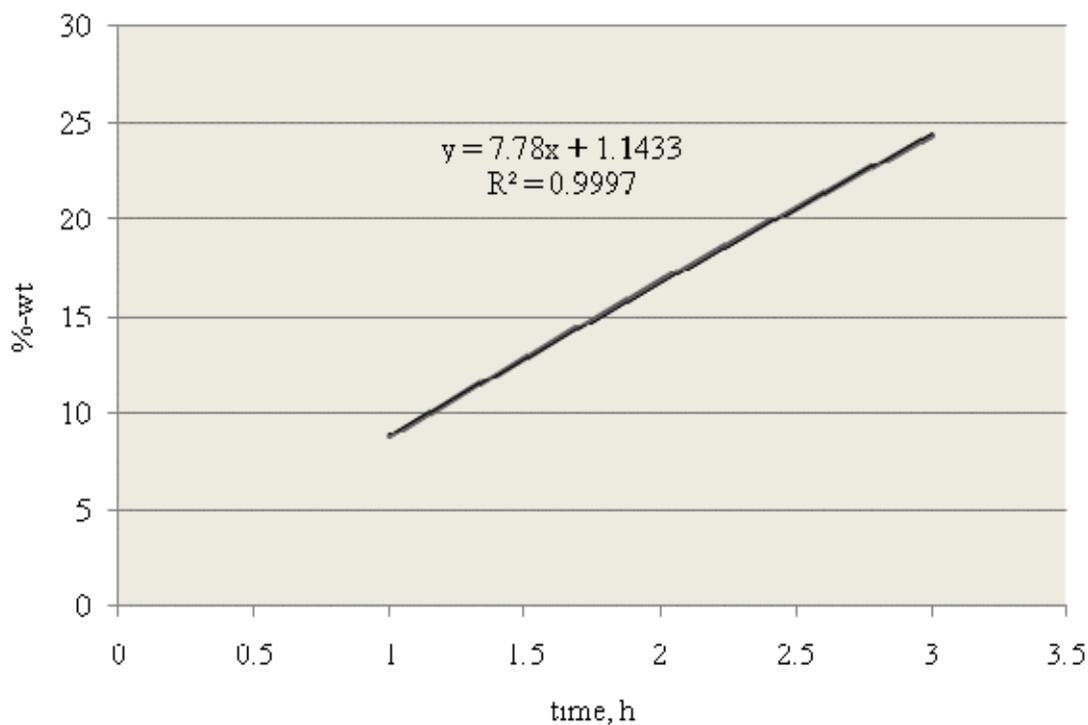
Figure 2.11 Effect of gas yields on the organic liquid product yields with respect to HT reaction time.

Figure 2.12 gives the respective liquid organic product oxygen content values by hour of reaction time performed with the MSU-1 catalyst. An ANOVA was performed with oxygen content as the independent variable and reaction time as the dependent variable. The ANOVA p-value was highly significant at 0.0001 which allowed performance of comparison of means tests. Comparisons of means test results are shown above the histogram for each reaction time hour in the Figure 3.13. The comparison of means results shows that oxygen content is highest at 19.6% for the 1 h reaction time. The 2 and 3 h reaction times produced significantly lower respective oxygen content values of 18.6 and 17.9 wt% which did not differ among themselves. Lowest oxygen content value was produced for the 3 h reaction time with a value of 17.86; this value was significantly lower than for all other hourly reaction times.
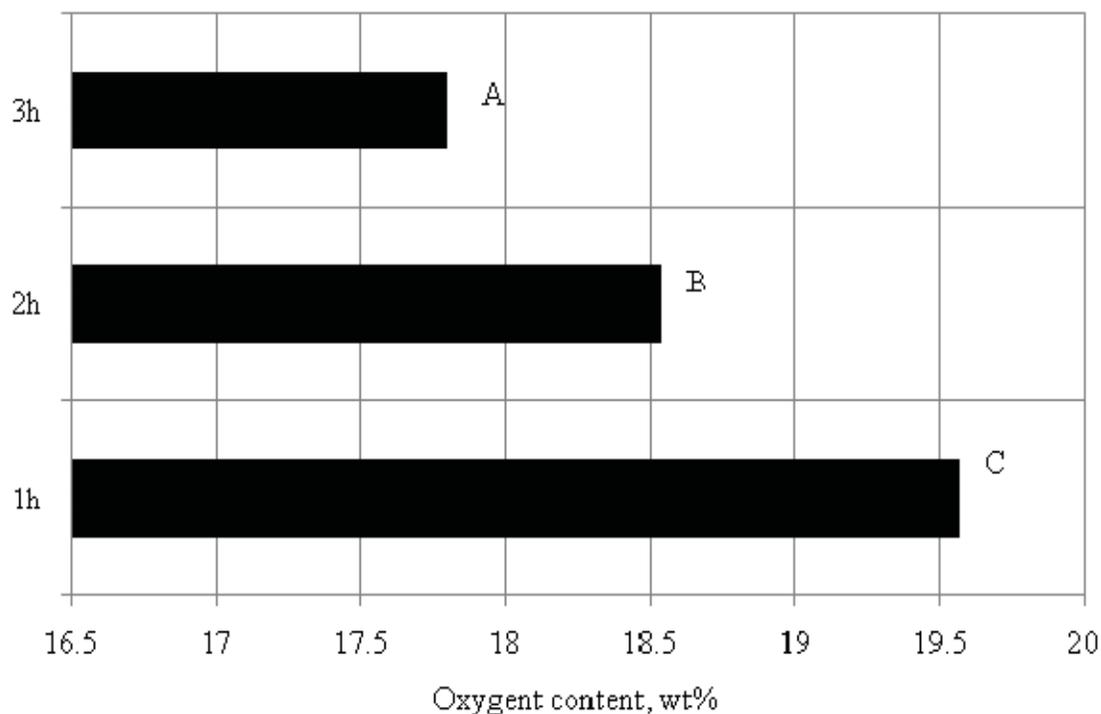
Figure 2.12   Comparison of oxygen content values for MSU-1 catalyst with respect to reaction time by ANOVA data analysis.

The experimental results from testing reaction times from 1 to 3 h show that organic product yields did not differ significantly for the 1 and 2 h reaction times. The reaction time of 3 h produced significantly lower yield compared to the 1 and 2 h reactions. Based on oxygen content values by reaction time the highest value was observed for the shortest 1 h treatment with a linear relationship of oxygen content as reaction time increased to 3 h. Based on oxygen content value, therefore, the 3 h treatment would provide a superior product but at respective losses of 2.2 and 6.2 percentage points of yield compared to the 1 h treatment. It is clear that selection of an optimum reaction time will depend on the use for which a hydrotreated product is intended. Direct input to a petroleum refinery is not practical for a biocrude with oxygen content of 19.6 wt%. If a second HC step is not to be performed it is clear that a longer

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reaction time must be employed. However, the loss of yield entailed in going to a 2 or 3 h reaction time may prohibit this choice.

If the biocrude is to be further cracked it may be immaterial that oxygen can be reduced with longer HT reaction times. If the HC step is performed and is highly effective in the final removal of oxygen the choice of a reaction time will likely be made on the criterion of highest yield. Finally, the biocrude produced by HT may be intended as a boiler fuel. In this case high higher oxygen content is not an issue and choice of reaction time would be determined by highest yield. Again, selection of the physical and chemical properties of all the product oils was given in Appendix A (Table A.2).

2.4.4   Catalyst regeneration studies with MSU-1 catalyst

Table 2.7 gives catalyst regeneration results for HT of bio-oil with MSU-1catalyst. From Table 2.7, when comparing the results of initial HT of bio-oil with the results of 4th regeneration experiment, it is observed that total organic liquid yields decreased only 2.5 wt% with almost no observed change in oxygen content. There was only a 1% increase in acid value and almost no change in the HHV occurred. From these observations, it is concluded that the MSU-1 catalyst is highly stable and active with respective to multiple regenerations and also effectively deoxygenates the raw bio-oil to produce a high-quality organic liquid.

Table 2.7   Comparison of organic liquid yield, oxygen content, acid value and HHV resulting from 4 regeneration of MSU-1 HT catalyst.

Property	Initial	1st regeneration	2nd regeneration	3rd regeneration	4th regeneration
Yields, wt%	41.22	40.33	41.03	39.19	38.72
Oxygen, wt%	19.55	19.28	19.40	19.97	19.78
Acid value, mg KOH/g	58.00	58.50	59.49	58.68	59.05
HHV , MJ/kg	33.12	33.4	33.23	33.21	33.23

2.4.5   Aging studies of raw bio-oil and HT organic liquid

Table 2.8 compares initial raw bio-oil and HT organic liquid viscosities after

aging at 40 ^{o}C over 6 h increments for a total of 24 h of aging. Initial raw bio-oil viscosity

was 10.15 cSt compared to 7.80 cSt for the HT product oil. The viscosity changes over

24 h for raw bio-oil were slight with highest viscosity of 10.73 cSt. This was a 5.7%

increase above the viscosity of the raw bio-oil prior to application of heat. Subsequent

viscosity changes over 24 h for the HT product oil were also negligible with highest

viscosity of 7.95 cSt demonstrated at 24h of 40 ^{o}C heating. This was only a 1% increase

in viscosity above the initial viscosity of the HT organic product. It is clear from these

results that the HT product oil is a highly stable organic product that could be stored and

shipped at ambient temperatures without substantial aging over time.

Table 2.8   Aging studies of raw bio-oil and HT organic product heated at 40 ^{o}C over 24
h and tested for viscosity initially and at 6 h increments.

	Viscosity of Raw bio-oil (cSt)	Viscosity of HT organic liquid (cSt)
0 h at 25°C	10.15	7.8
6 h at 40°C	10.2	7.91
12 h at 40°C	10.3	7.93
18 h at 40°C	10.58	7.93
24 h at 40°C	10.73	7.95

2.4.6   Comparison of physical and chemical properties of raw bio-oil and the HT organic product

Table 2.9 summarizes the physical and chemical properties of raw bio-oil and the

HT organic product produced by MSU-1 catalysis. From Table 2.9, it is clear that there is

a significant difference between physical and chemical properties of raw bio-oil and the HT organic product. The major differences are observed in terms of acid value, water content, oxygen content and HHV. The HT organic product had an acid value of 58 which is a 40% reduction when compared with the raw bio-oil acid value of 95. The HT organic product density of 0.95 g/mL is 20% less than the 1.2 g/mL density of raw bio-oil. The oxygen content of the HT organic product, at 19.6 wt%, is 44% less than the raw bio-oil oxygen content (43.5 wt%). HT organic product pH was increased to 4.10 above the 2.3 pH of raw bio-oil. Raw bio-oil HHV was 17.1 MJ/kg compared to the 33.12 MJ/kg value for the HT organic product. Finally, the water content of HT organic liquid was reduced to 5.0 wt% compared to the 23.5 wt% value for raw bio-oil, a nearly 200% reduction. The chemical and physical results from the HT treatment of bio-oil with the MSU-1 catalyst indicate a very significant upgrading in fuel-related properties.

Table 2.9   Physical and chemical properties of raw bio-oil and HT of bio-oil.

Properties	Raw bio-oil	HT organic liquid
Acid value, mg KOH/g	95.0	58.0
Density, g/mL	1.2	0.95
Oxygen, wt%	43.5	19.6
HHV, MJ/kg	17.1	33.12
Water, wt%	23.5	5.00
pH	2.30	4.10

2.4.7   Calculation of hydrogen consumption of energy efficiency of the HT process

Hydrogen consumption could not be calculated accurately in the high-pressure batch autoclave set-up. However, for all the experiments mass balances, gas phase compositions and elemental analysis were determined experimentally and allowed a

rough computation of hydrogen consumption. Calculations were performed for the HT of raw bio-oil with MSU-1 catalyst at 350 °C for 1 h under 1500 psig of H_2 pressure. On the basis of equation 2.1, Actual hydrogen consumption was calculated to be 433 NL/kg dry bio-oil. From the previous literature, up to 5 wt% of hydrogen is required on a bio-oil weight basis, which is approximately 600 NL/kg dry bio-oil. Based on the above statement, for HT process MSU-1 catalyst uses 27% less hydrogen than the previously reported literature [10, 15, 17]. The calculation sheet for hydrogen consumption is given in Appendix A (A.1).

A simplified schematic HDO chemical reaction is shown in Eq. 2.1 below.

$$-(CHO)- \ + \ H_2 \ \longrightarrow \ -(CH)- \ + \ (H_2O, CO_2, CH_4, CO) \qquad \text{(Eq. 2.1)}$$
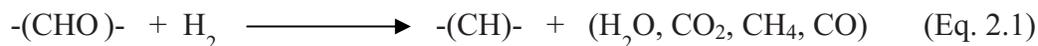
Energy efficiency of the HT process can be calculated with Equation 2.2;

$$Energy \ efficiency = X_{HT.} \ \frac{HHV_{product}}{HHV_{bio\text{-}oil}} \ . 100\% \qquad \text{(Eq. 2.2)}$$

Where,

X_{HT}: HT product oil yield = 41.22 wt% of total product

$HHV_{product}$: Heating value of HT organic liquid = 33.12 MJ/kg

$HHV_{bio\text{-}oil}$: Heating value of raw bio-oil = 17.10 MJ/kg

The result of applying this equation indicates that the energy efficiency of the HT process with MSU-1 catalyst is 80%. This energy efficiency value for the HT process with MSU-1 catalyst correlates with the previously reported literature values [17].

2.5   Product analysis

To gain insight in the reactions occurring during the bio-oil HT reaction, the raw bio-oil and product oil was analyzed by GC/MS, ^{1}H-NMR and FTIR.

2.5.1   GC/MS analysis of raw bio-oil and HT organic liquid

Bio-oil obtained from fast pyrolysis of loblolly pine feedstock is a multi component mixture and contains hundreds of reactive chemical compound types [3,9-10]. A representative GC/MS chromatogram of raw bio-oil is provided in Figure 2.13. A second chromatogram of the HT organic fraction is given in Figure 2.14. As expected, it is clearly evident that the spectra of Figure 2.14 differ a great deal from that for the spectra for the original raw bio-oil in Figure 2.13.
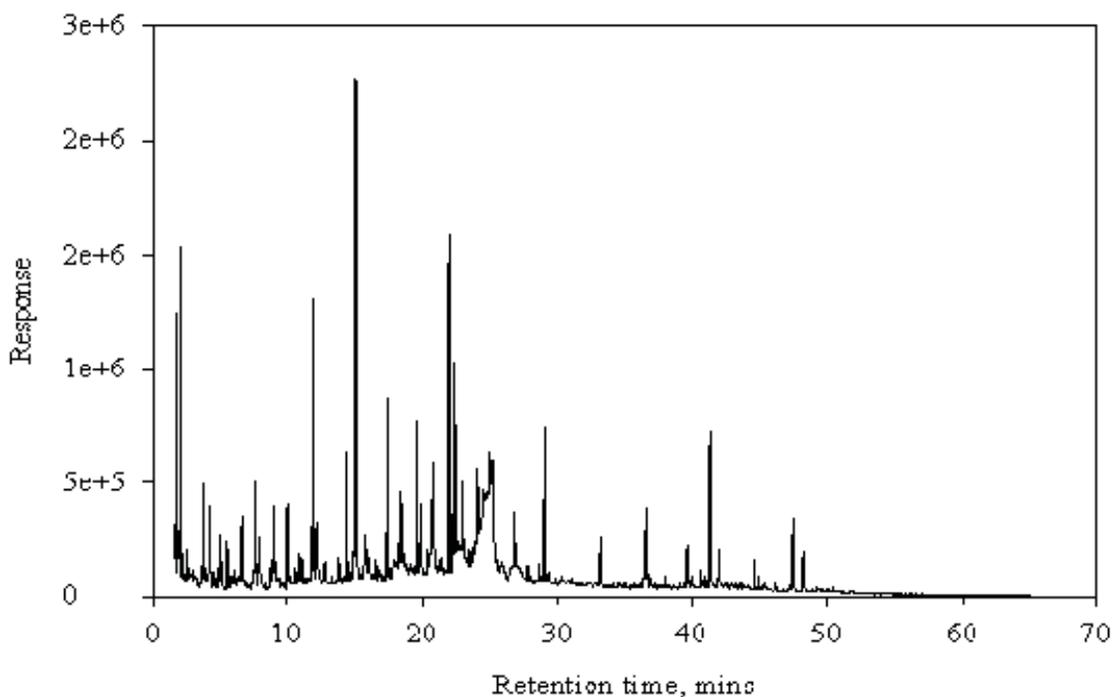
Figure 2.13   GC/MS chromatograph of raw bio-oil produced from fast pyrolysis of loblolly pine feedstock.
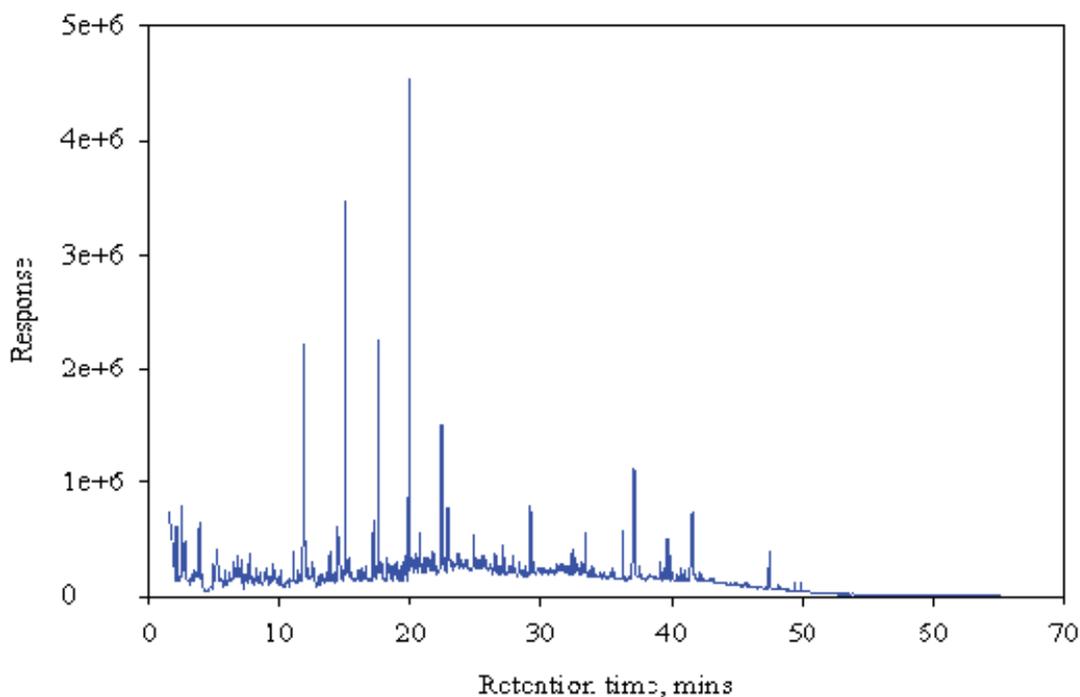
Figure 2.14   GC/MS chromatograph of HT organic liquid from raw bio-oil with MSU-1 catalyst (at temperature 350 ^{o}C, with 1500 psig of H_2 gas for 1h reaction time).

In Table 2.10 the most abundant target compounds identified by GC/MS in both raw bio-oil and the HT organic product are compared. In raw bio-oil, phenols and its derivatives are major oxygenated compounds [13]. Besides phenolic compounds, a high percentage of compounds derived from carbohydrates such as oleic acid, acetic acid, hydroxyl acetaldehyde, hydroxyl acetone, ethyl acetate, 1-hydroxy-2-butanone, 5-hydroxymethyl furfural and levoglucosan are present. In the HT organic fraction it is evident that most of the phenolics, aldehydes, acids and carbohydrates present in raw bio-oil are converted during the HT process. This is also evident from the presence of high percentage of methylated phenols such as 3-methylphenol, 2-methoxyphenol, 2-methoxy-4-methylphenol, 4-ethyl-2-methoxyphenol and 2-methoxy-2-propylphenol. These are likely to be produced from hydrogenation of phenolic compounds from the lignin fraction

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present in bio-oil [34]. Oleic acid, furfural, furfuryl alcohol, phenol, trans-isoeugenol,

acetovanillone and levoglucosan have been completely eliminated from the HT treatment

of the raw bio-oil. These compounds are likely to have been converted to low molecular

weight hydrocarbons. Table 2.11 gives all identified GC/MS non-target compounds for

HT organic product. The table shows that, In addition to the formation of methylated

phenols, a high percentage of aliphatic hydrocarbons and cyclic aliphatic hydrocarbons

were also formed. These are likely to have been formed by the subsequent reaction of

phenolics and alkyl benzenes with hydrogen. Decanoic acid and its derivatives are high-

molecular weight compounds and it was unexpected to observe that they formed during

the HT reaction. A possible explanation is the conversion of oleic acid from the catalyzed

hydrogenation reaction.

Table 2.10   GC/MS comparison of raw bio-oil and HT organic liquid in terms of relative concentration by compound type.

Qunatitated target compounds	retention time, mins	quantitation ion	Concentration (%)	
			Raw bio-oil[a]	HT organic liquid[b]
Furfural	3.84	96	0.47	0.00
Furfuryl alcohol	4.30	98	0.14	0.01
2-methyl-2-cyclopentenone	5.78	96	0.00	0.00
2 (5H)-furanone	6.22	84	0.06	0.02
5-methylfurfural	7.50	110	0.00	0.00
3-methyl-2-cyclopentenone	7.93	96	0.02	0.03
Phenol	8.73	94	0.16	0.00
3-methyl-1,2-cyclopentaned	9.97	112	0.74	0.01
2-methylphenol	10.93	108	0.09	0.00
3-methylphenol	11.78	108	0.13	0.53
2-methoxyphenol	11.88	124	0.72	1.28
2,6-dimethylphenol	12.46	122	0.01	0.03
2,4-dimethylphenol	13.81	122	0.05	0.00
3-ethylphenol	15.02	122	0.04	0.03
2,3-dimethylphenol	14.79	122	0.01	0.06
Naphthalene	14.49	128	0.00	0.00
2-methoxy-4-methylphenol	15.09	138	1.06	1.95
1,2-benzenediol	15.62	110	0.00	0.00
3-methyl-1,2-benzenediol	17.20	124	0.01	0.01
4-ethyl-2-methoxyphenol	17.55	137	0.27	1.42
4-methyl-1,2-benzenediol	18.12	124	0.01	0.01
2,6-dimethoxyphenol	19.58	154	0.01	0.01
Eugenol	19.61	164	0.17	0.00
2-methoxy-4-propylphenol	19.95	137	0.07	1.61
Vanillin	20.67	151	0.00	0.02
cis-Isoeugenol	20.99	164	0.13	0.01
3,4-dimethylbenzoic acid	21.16	105	0.01	0.01
trans-Isoeugenol	22.01	164	0.50	0.00
4-ethylresorcinol	21.82	123	0.00	0.01
Levoglucosan	23.73	60	0.35	0.02
Acetovanillone	22.89	166	0.14	0.01
Oleic acid	36.51	55.00	0.83	0.01

[a]The bio-oil was produced by fast pyrolysis in an auger reactor at 450 ^{o}C from southern pine as feedstock[7, 8].
[b]The bio-oil was upgraded with MSU-1 catalyst at 350 ^{o}C for 1 h.

Table 2.11   Non-target compounds from GC/MS spectra of HT process with MSU-1 catalyst.

quantitated non-target compounds in HT organic liquid[a]	retention time, mins [b]	concentration (%)
cyclopropane, butyl-	2.53	0.14
cyclopentanone	2.80	0.19
pentanoic acid, methyl ester	3.51	0.15
cyclopropane, propyl-	4.88	0.18
heptane, 3,3,5-trimethyl-	5.24	0.51
cyclopentanone, 2,4-dimethyl-	5.55	0.13
butanoic acid, ethyl ester	6.55	0.31
cyclopentanone, 2-ethyl-	6.84	0.29
cyclohexanone, 2-methyl-	7.06	0.13
butane, 1-cyclopropylidene-5-(tetra)	7.71	0.19
acetic acid, hexyl ester	9.53	0.22
phenol, 2-methyl-	11.07	0.19
phenol, 4-ethyl-	14.57	0.28
phenol, 2-propyl-	17.12	0.27
4-hepten-1-ol	17.80	0.17
tridecanoic acid, methyl ester	32.51	0.13
n-hexadecanoic acid	33.35	0.16
octadecanoic acid	37.08	0.43
benzeneamine, 3-ethyl-4-hydroxy	43.18	0.43
bi-1-cycloocten-1-yl	49.85	0.12

[a]100 g raw bio-oil;5 g MSU-1 catalyst;1500 psig H_2 at 350 ^{o}C for 1 h
[b]These results should be interpreted with reservation as the GC/MS library is not 100% reliable.

2.5.2   FTIR analysis of bio-oil and HT organic liquid

Figure 2.15 gives an FTIR spectral comparison of the functional groups contained in raw bio-oil, the HT organic product and petroleum diesel. In HT organic liquid IR spectrum the broad absorbance band between 3050 and 3600 cm^{-1} are ascribed to $\gamma(O-H)$ vibrations of hydroxyl groups which indicate the presence of alcohols, phenols and water in the raw bio-oil. In the case of the HT organic liquid this peak is observed with reduced intensity confirming the reduction of phenolic and alcoholic groups.HT organic liquid In raw bio-oil the presence of -OH absorbance peak together with the presence of C=O stretching vibrations between 1650 and 1750 cm^{-1} indicates the presence of carboxylic acids, ketones, quinines, aldehyde groups and their derivatives; these peaks are also present in the HT organic product spectrum with reduced peak levels. This is also confirmed by the acid value of 58 for the HT organic product and this value is approximately 40 percentage points less when compared with the acid value of raw bio-oil which is 94 (Table 2.9).

Further, the HT organic product demonstrates sharp spectral peaks at 3000-2800cm^{-1} and 1500-1400cm^{-1}. These peaks confirm the presence of aliphatic hydrocarbons in HT organic liquid and, in addition, the peaks also correlate with aliphatic hydrocarbon peaks (2923 and 1457cm^{-1}) present in petroleum diesel fuel. The peaks identifying aliphatic hydrocarbons in the HT organic liquid product indicate a significant increase when compared with raw bio-oil.
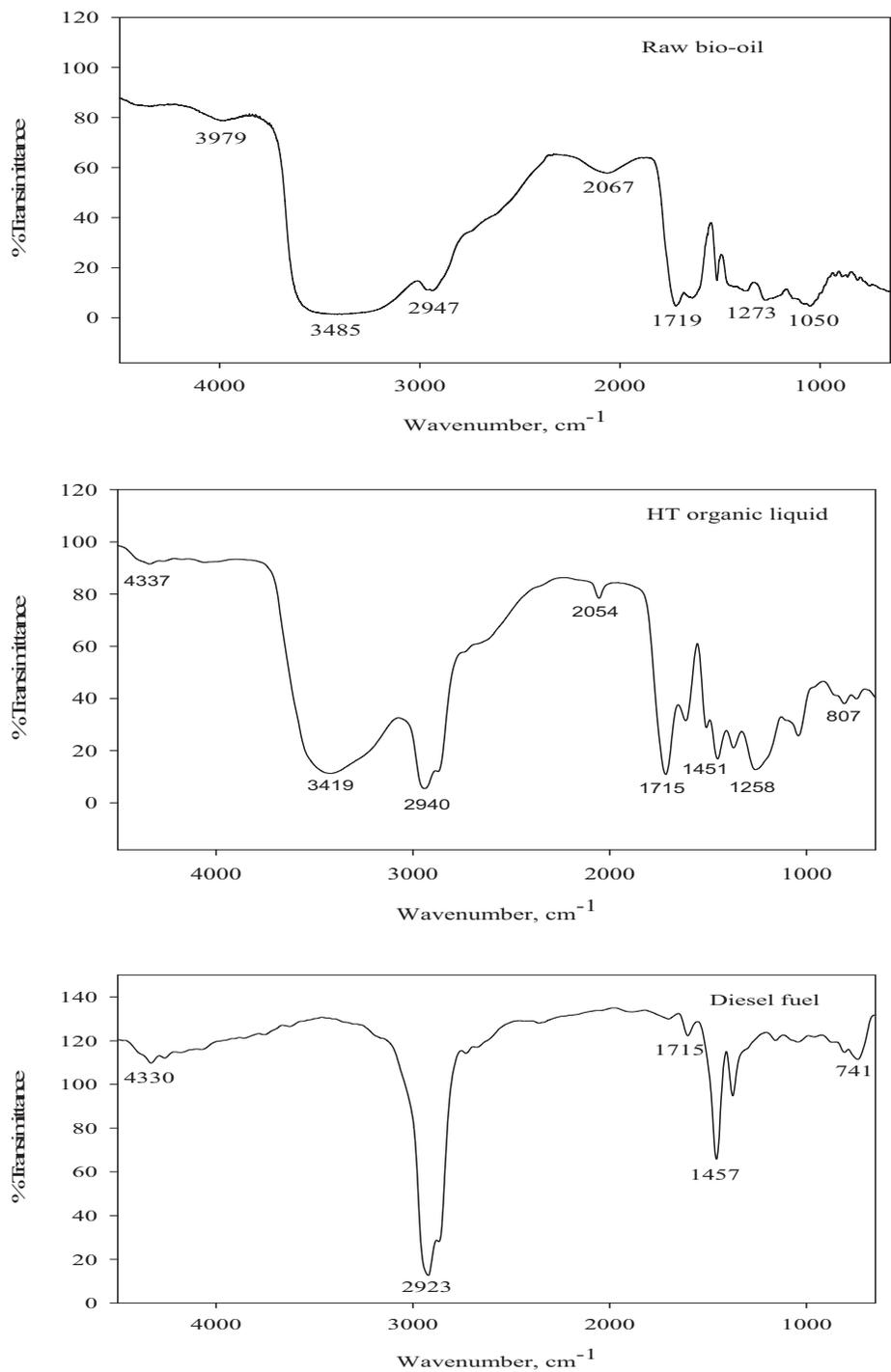
Figure 2.15   FTIR spectral comparisons of (a) raw bio-oil, (b) HT organic liquid, and (c) diesel fuel.

2.5.3   NMR analysis of raw bio-oil and HT organic liquid

^{1}H-NMR spectra of raw bio-oil and HT organic liquid are shown in Figures 2.16 (a) and (b) respectively. From Figures 2.16 (a) and (b) it is evident that there is a significant difference between ^{1}H-NMR spectrum of raw bio-oil and HT organic liquid spectrum. In raw bio-oil ^{1}H-NMR spectrum aliphatic protons occurs between 0.0 to 1.5 ppm along with aliphatic hydroxyl groups. But in contrast in HT organic liquid spectrum at 0.0 to 2.5 ppm saturated aliphatic hydrocarbons are formed, which is also confirmed by GC/MS analysis. Protons attached in alpha position to ketone, aldehydes or carboxyl groups and benzylic protons which occur from 2.2 to 3.0 ppm are present in raw bio-oil and these peaks are significantly decreased in HT organic liquid spectrum. Phenols and phenolic derivates present in raw bio-oil spectrum occur between 4 to 8ppm, and these peaks reduced to a significant amount in HT organic liquid spectrum. The region between 4.2 to 6.4 ppm represents aromatic ether protons (i.e., lignin derived methoxy phenols) and also compounds related to carbohydrate fraction; these are very significant in raw bio-oil and these peaks also present in HT organic liquid but with less resolution. In both ^{1}H-NMR spectra of raw bio-oil and HT organic liquid spectrums aromatics groups are observed between 6.5 to 8 ppm. Figure 2.18 shows the ^{1}H-NMR spectrum of aqueous fraction obtained during the HT process with MSU-1 catalyst. In Figure 2.17 it is identified that there are no significant amounts of organic compounds except very low quantities of phenolic compounds (3.2 ppm) and mostly water (1.6ppm) are present. A sharp peak at 4.5-5 ppm represents the solvent D_2O, which is used for dissolving the aqueous fraction prior to the analysis.

From the ^{1}H-NMR analysis, it was observed that ^{1}H-NMR spectra of raw bio-oil and HT organic liquid spectrums are significantly different. HT organic liquid spectrum contains aliphatic hydrocarbon region and also reduced phenolic groups are observed.
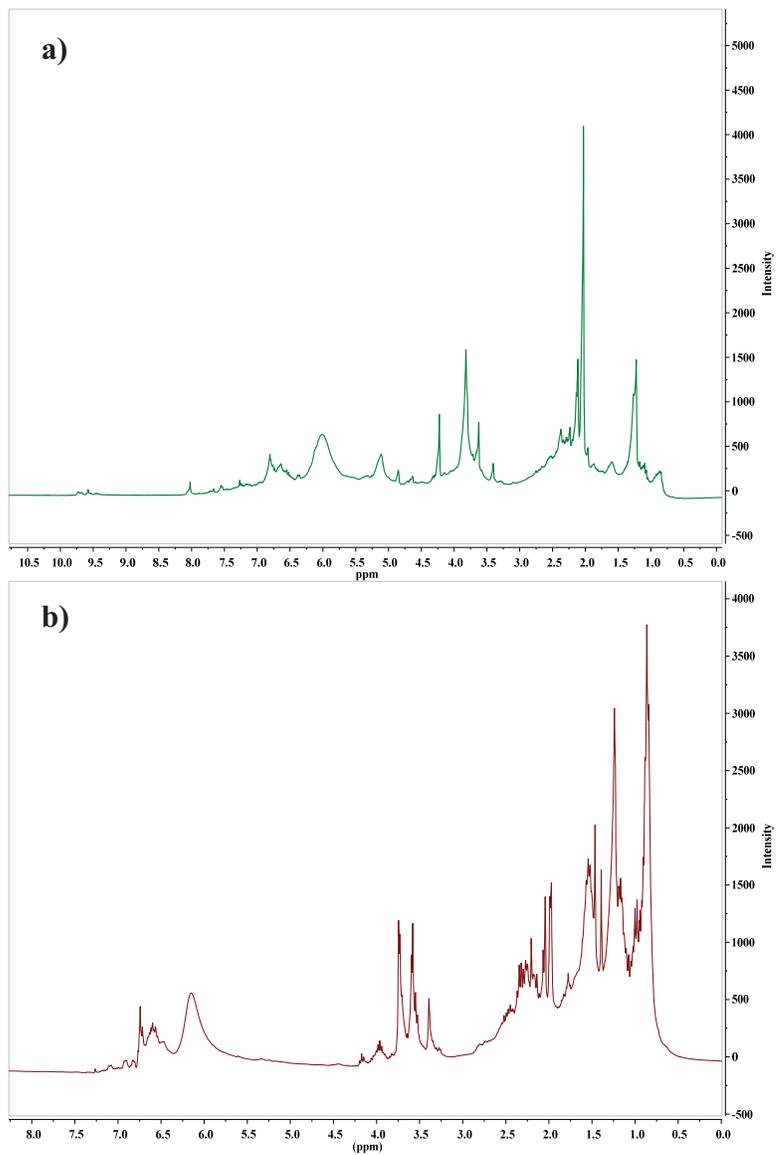
Figure 2.16 ^{1}H- NMR spectra of (a) raw bio-oil and (b) HT organic liquid (Bruker 300 MHz, CDCl$_3$ as solvent).
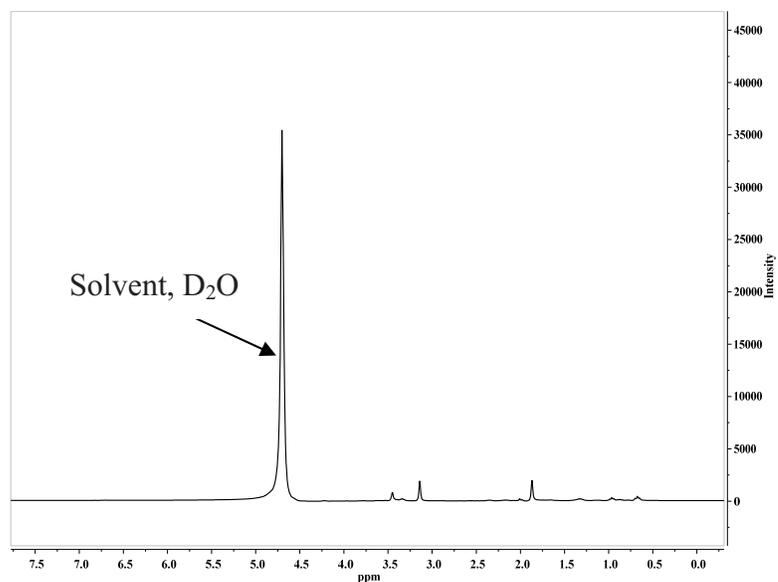
Figure 2.17 ^{1}H- NMR spectrum of water fraction obtained after the HT of bio-oil
(Bruker 300 MHz, D$_2$O as solvent).

The full potential of NMR to gain information on the nature of HDO oils needs to

be explored but it is evident that it could become a great analytical tool for identifying the

nature of these oils in molecular level and to explore their potential properties.

2.6   Summary

This chapter describes an experimental study on the HT of bio-oil with the

objective to produce partially deoxygenated oil with properties similar to boiler fuel or

No.2 diesel fuel. The HT experiments were performed in a high-pressure batch autoclave.

Catalyst screening experiments were performed using six commercially available

heterogeneous catalysts and one proprietary catalyst. Among all the hydrotreating

catalysts tested, proprietary MSU-1 catalyst shows superior catalytic activity in terms of

highest organic liquid yield (38 wt%), organic liquid contains highest H/C ratio (1.65)

and the second best low oxygen content (16.5 wt%). This was also further evident by the

ANOVA statistical data analysis. Further, as a typical hydrotreating catalyst (NiMo/Al

and CoMo/Al) MSU-1 does not need any presulfidation or sulfur in the feed prior to usage, and also it is 90% more cost effective than the heterogeneous precious noble metal catalysts, thereby reducing the capital cost needed for hydrotreating catalyst in the mild hydrotreating process of bio-oil.

Later, HT process optimization studies with MSU-1 catalyst were performed with respect to temperature and reaction time. From the optimization studies it was found that a temperature of 350 $^{\circ}$C is sufficient to produce a light oil with the oxygen content of 17wt%, and also the reaction time of 1h is sufficient to produce high organic liquid yield of 41.2wt% with the oxygen content of 19 wt%. The calculated energy efficiency of the hydrotreating of bio-oil with MSU-1 catalyst is approximately 80%. From catalyst regeneration studies it was found that MSU-1 catalyst is highly stable and active with respect to multiple regenerations and is also effective in deoxygenation of the bio-oil to produce a quality organic liquid. Hydrogen consumption of HT process is about 433 NL/kg dry bio-oil. This value is approximately 27% less than the previously reported literature value.

When compared with raw bio-oil the hydrotreated organic liquid contains 45% less acid value, 60% less oxygen, 78% less water content and higher heating value of twice that of the raw bio-oil. GC-MS analysis show reduced acids, phenols, aldehydes and ketones when compared with raw bio-oil and new hydrocarbon compounds are also formed. FTIR spectral data clearly distinguish the difference between raw bio-oil and hydrotreated organic liquid and similarities with diesel fuel were also observed. It is also shown from the 1H-NMR spectra of hydrotreated organic liquid that formation of aliphatic hydrocarbons is evident.

The hydrotreated organic liquid described should be able to be used as boiler fuel with minimal modifications. In addition, it appears very feasible that it can be produced with a cost effective heterogeneous catalyst with optimized HT process.

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CHAPTER III

HYDROCRACKING OF HYDROTREATED BIO-OIL FOLLOWED BY

FRACTIONAL DISTILLATION OF THE RESULTING LIQUID

HYDROCARBON MIXTURE

3.1   Introduction

The need for renewable sources of energy has motivated increased research

efforts directed towards the development of pyrolysis oil, also called bio-oil, as a liquid

fuel and source of useful chemicals [1-3]. However, bio-oils from fast pyrolysis contain

high levels of oxygen compounds that need to be removed to improve the stability of the

liquid fuels. A variety of upgrading technologies have been proposed, of which catalytic

hydroprocessing of bio-oil has received considerable attention [4]. Catalytic

hydroprocessing of bio-oil with a catalyst in hydrogen atmosphere converts the oxygen

contained in the oxygenated compounds present in bio-oil to H_2O and CO_2 as well as

forming saturated C-C bonds [5]. Typically harsh conditions such as 300-400 ^{o}C are

required to obtain a product with properties similar to, or within the range of,

transportation fuels [6]. This process is known as hydrodeoxygenation (HDO).

HDO is similar to the hydrodesulfurization (HDS) process applied in petroleum

refining of high sulfur crude oils [4]. An important early discovery by Elliot et. al is the

value of utilizing a two-stage process to fully hydroprocess bio-oils to hydrocarbons [4,

7-9]. It was found that the hydrocracking (HC) step to produce hydrocarbons must be

preceeded by a mild hydrotreating (HT) step to prevent the coking that occurs when raw bio-oil is subjected to an elevated temperature.

Researchers found that application of a first-stage HT applied under mild conditions (140-275 $^{\circ}$C) hydrogenated thermally unstable bio-oil compounds without decomposition. Elimination of the thermal decomposition of unstable compounds reduced catalyst coking. The organic product of the mild HT step produced a stabilized bio-oil with moderately reduced oxygen content accompanied by removal of most of the water and acid compounds contained in the bio-oil. A second-stage HC step was found to be successfully applied to the stabilized, low water content bio-oil. The typical HC temperatures of 300-450°C could be applied without undue coking of the catalyst and produced a product with sharply reduced oxygen content [4, 5, 11, 12]. Most of this work has been focused on using sulfided CoMo/Al and NiMo/Al based catalysts [11, 12]. Noble metal catalysts have recently also gained attention for the hydroprocessing of bio-oil due to their known high hydrogenation activity without need of pre-sulfiding prior to catalysis [13].

Chapter II screened six commercial and one proprietary catalyst for bio-oil HT efficacy. The best performing catalyst, MSU-1, was selected to optimize in terms of best temperature and time of reaction. At the optimum conditions the MSU-1 catalyst successfully hydrotreated raw bio-oil to produce an organic liquid product with the characteristics described in Table 3.1.

Table 3.1 summarizes the physical and chemical properties of raw bio-oil and the HT organic product produced by MSU-1 catalyst. From this table it is clear that there is a significant difference between physical and chemical properties of raw bio-oil and the HT organic product. The major differences are observed in terms of acid value, water

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content, oxygen content and HHV. The HT organic product had an acid value of 58

which is a 40% reduction when compared with the raw bio-oil acid value of 95. The HT

organic product density of 0.95 g/mL is 20% less than the 1.2 g/mL density of raw bio-

oil. The oxygen content of the HT organic product, at 19.6 wt%, is 44% less than the raw

bio-oil oxygen content (43.5 wt%). HT organic product pH was increased to 4.10 above

the 2.3 pH of raw bio-oil. Raw bio-oil HHV was 17.1 MJ/kg compared to the 33.12

MJ/kg value for the HT organic product. Finally, the water content of HT organic liquid

was reduced to 5.0 wt% compared to the 23.5 wt% value for raw bio-oil, a nearly 200%

reduction. The chemical and physical results from the HT treatment of bio-oil with the

MSU-1 catalyst indicate a very significant upgrading in fuel-related properties.

Table 3.1   Physical and chemical properties of HT organic liquid produced by catalysis
            with MSU-1 catalyst.

Property	Raw bio-oil	HT organic liquid
Acid value, mg KOH/g	95.0	58.0
Density, g/mL	1.2	0.95
Oxygen, wt%	43.5	19.6
HHV, MJ/kg	17.1	33.12
Water, wt%	23.5	5.00
pH	2.30	4.10

The main objective of this study was to develop and optimize application of a HC

catalyst that will process a HT organic liquid and produce a zero oxygen pure

hydrocarbon mixture. A second objective was to determine the physical and chemical

characteristics of the mixed hydrocarbons produced. A third objective was to perform

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fractional distillation of the HC hydrocarbon mix by fuel weights equivalent to the most frequently used petroleum fuel weights.

3.2   Materials and methods

3.2.1   Hydrotreated bio-oil as a starting material

The HT bio-oil that will be used HC in this study was produced by catalysis with the MSU-1 catalyst described in Chapter II. The HT product was produced in a high pressure batch autoclave containing 100 g of raw bio-oil; 5 wt% of MSU-1 catalyst; reaction temperature of 350 ^{o}C; autoclave hydrogen pressure of 1500 psig; with stirring at 1000 rpm for 1hr. Physical and chemical properties of the HT bio-oil are given in Table 3.1.

3.2.2   Catalysts

Various catalysts have been reported for the HC bio-oils (4, 5, 14-16]. In this study, two commercially available HC catalysts, sulphided NiMo/Al and CoMo/Al [4, 15, 17], and a proprietary MSU-2 catalyst were selected.

3.2.3   Chemicals and gases

Acetone, methanol and hexane were obtained from sigma-Aldrich. Dimethylsulfoxide (DMSO) solution obtained from Gaylord chemicals. Ultra high purity hydrogen (>99.99%) and helium (>99.99%) gases were supplied by Nex-Air.

3.2.4   Experimental procedure for HC process and analytical methods

HC of stabilized bio-oil was performed in a 450 mL high-pressure batch autoclave (Parr Instruments Co). The maximum pressure and temperature achievable by the autoclave is 5000 psig and 500 ^{o}C, respectively. The autoclave is equipped with an

electrical heating/cooling system for control of the autoclave temperature. Two input gas valves are available to allow input of two gas types simultaneously if desired. Reaction exit gas is expelled by a valving system.

The reactor was filled with HT organic liquid (50 g) and catalyst at a 10 wt% on basis of HT organic liquid. Subsequently, the reactor was flushed three times with helium gas and pressurized with 1000 psig of hydrogen gas at room temperature. The reactor was heated to the 400 ^{o}C at a heating rate of 10 ^{o}C/min and kept at that temperature for 2 h. The reactor contents were stirred at 1000 rpm with a magnetically driven stirrer controlled by a digital control box.

The autoclave pressure developed during the HC process was recorded at 15 min intervals for each temperature tested. The final autoclave pressure was recorded for the mass balance calculation and the gas phase was sampled with a 1-liter SKC gas sampling bag. Following each 2 h reaction the reactor was cooled to ambient temperature and the liquid product of the autoclave was collected. Following the HC catalytic treatment the liquid product consisted of two phases: an organic phase and an aqueous phase. The total liquid product was centrifuged with a Fisher Accuspin-3R at 4000 rpm for 2 h at 10 ^{o}C to obtain a clean separation of the organic and water phases. Following centrifugation the organic phase floated on the water phase allowing siphoning of the water with a Buckner funnel.

Following the reaction and removal of the product from the reactor residual solids were present on the reactor walls. Also, a small amount of char was present at the bottom of the separated phases following centrifugation. This char was maintained in the centrifuge tube when the organic and liquid phases were poured into the Buchner funnel. The solids cleaned from the reactor walls and the solids collected from the bottom of the

centrifuge tube were both combined and subsequently washed with acetone and dried at 100 ^{o}C overnight. The separated char, organic fraction and aqueous fraction were weighed to determine the total weight of product resulting from the hydrocracking.

To eliminate mass transfer effects, CoMo/Al and NiMo/Al catalyst pellets were crushed into a fine powder prior to their usage. Presulfiding of CoMo/Al and NiMo/Al catalysts were performed by mixing the catalysts with 2 wt% of dimethyl sulfoxide at 240 ^{o}C for 3 h in 1000 psig of H_2 pressure.

3.2.5 Procedure for optimization of reaction time for MSU-2 catalyst

The HC process was further optimized for the MSU-2 catalyst to attempt to obtain higher organic liquid yields with lower oxygen content with respect to reaction time using the variables as shown in Table 3.2. The reaction time ranged between 1-4 h with 1 h intervals; H_2 pressure was 1000 psig and temperature was 400 ^{o}C; HT organic liquid and MSU-2 catalyst were applied at 50 and 5 g, respectively.

Table 3.2   Variables applied during the optimization of temperature and reaction time for MSU-2 catalyst.

Variables	Effect of reaction time
Time, hr	1, 2, 3 and 4
H_2 pressure, psig	1000
Temperature, ^{o}C	400
Stabilized bio-oil, g	50
Catalyst, g	5

3.3   Analysis of raw and upgraded bio-oils

3.3.1   Physical properties

HT organic liquid and HC hydrocarbon densities were determined by using Anton Parr DMA 35n portable density meter. Viscosities were determined by Ubbelohde capillary viscometer at 40°C water bath temperature. Kinematic Viscosity was measured by multiplying flow time of the liquid with a calibration constant (0.02986) for the viscometer. Flash point was tested by Koehler flash point tester model no.K16200. Higher heating value (HHV) was determined by Ika-5000 bomb calorimeter. Lower heating value (LHV) was calculated from the HHV and the total weight percent of hydrogen obtained from bio-oil elemental analysis [7, 18].

The acid value was determined by dissolving 1 g of bio-oil in a 50:50 isopropoanol/water mixture and titrating to a pH of 8.5 with 0.1N KOH. The acid values were calculated as the number of milligrams of KOH equivalent to 1 g of sample. The pH values determined by adding 1 g of bio-oil to 50 mL of water, stirring, and measuring the pH with an Orion Model EA920 pH meter. Elemental carbon, hydrogen, nitrogen were determined by EAI CE-440 elemental analyzer and oxygen content was determined by difference. Water content of the bio-oil was determined by the Karl-Fisher titration using standard methods [19, 20].

3.3.2   Chemical analysis

A sample of hydrocarbon mix from the HC process was sent to a third party lab for the detailed hydrocarbon analysis (DHA). Simulated distillation studies were carried out using Agilent 6890 GC with standard ASTM D2887 procedure.

Fourier transform infrared (FTIR) spectra wad done by Varian 3500 FTIR analyzer with standard potassium bromide disk technique and spectra were analyzed using Varian-Resolutions software. Proton-nuclear magnetic resonance (^{1}H-NMR) appears to be a useful technique for bio-oil characterization [7]. ^{1}H-NMR spectra were recorded on a 300 MHz NMR (Bruker) instrument and spectral interpretation is done by using TOPSPIN 2.1.6 version software. For ^{1}H-NMR all samples were dissolved in solution of $CDCl_3$ except water phases obtained from HC experiments which were dissolved in D_2O.

A Varian CP-4900 Micro Gas Chromatograph analyzed the gas composition of the remaining gas stream after each batch experiment. There are totally 4 independent GC channels in Varian CP-4900 Micro Gas Chromatograph system. Channel No.1, which has a 10 meters MS5A GC column, was utilized to analyze hydrogen, oxygen, nitrogen, methane, and carbon monoxide concentration. Channel No.2, which is equipped with a 10 meters PPQ GC column, was utilized to test the concentration of carbon dioxide and ethane. The Micro Gas Chromatograph gas analysis conditions for this study are given in Table 3.3.

Table 3.3   Micro GC conditions for gas phase analysis of gases collected after the HT batch runs.

Channel No.	Injector Temperature (^{o}C)	Column Pressure (psig)	Column Temperature (^{o}C)	Sample Time (s)	Injection Time (ms)
No. 1	50	20	80	60	40
No. 2	110	20	60	60	40

3.3.3 Fractional distillation of hydrocarbon mix

Fractional distillation of hydrocarbon mix was performed using 36-100 Spinning Band Distillation System purchased from BR Instruments Corporation, Easton, MD. Maximum heat capacity of this distillation system is around 225 ^{o}C at atmospheric pressure. To achieve temperatures greater than 225 ^{o}C vacuum is applied to the distillation system to increase the boiling range distribution of the sample and decrease the pressure drop during the distillation. The distillation of hydrocarbon mix was performed at various temperatures (0 to 350 ^{o}C) depend on the boiling range distribution of the hydrocarbon mix obtained from HC process.

3.4 Results and discussion

3.4.1 Catalyst screening studies for HC experiments

Figure 3.1 shows the mass balance results from HC catalysis performed by MSU-2, CoMo/Al and NiMo/Al catalysts. For all the three catalysts the organic fraction was lighter than water and, as a result, it floated on the aqueous fraction. The yield of organic fraction ranged from 66 to 68 wt%. The significantly highest organic yield was obtained for MSU-2 catalyst at 68 wt%. The respective yields for CoMo/Al and NiMo/Al catalysts were 66.0 and 66.2 with these yields significantly lower than those for MSU-2. The yields for CoMo/Al and NiMo/Al did not differ significantly between themselves and produced almost similar yields (66 wt%).
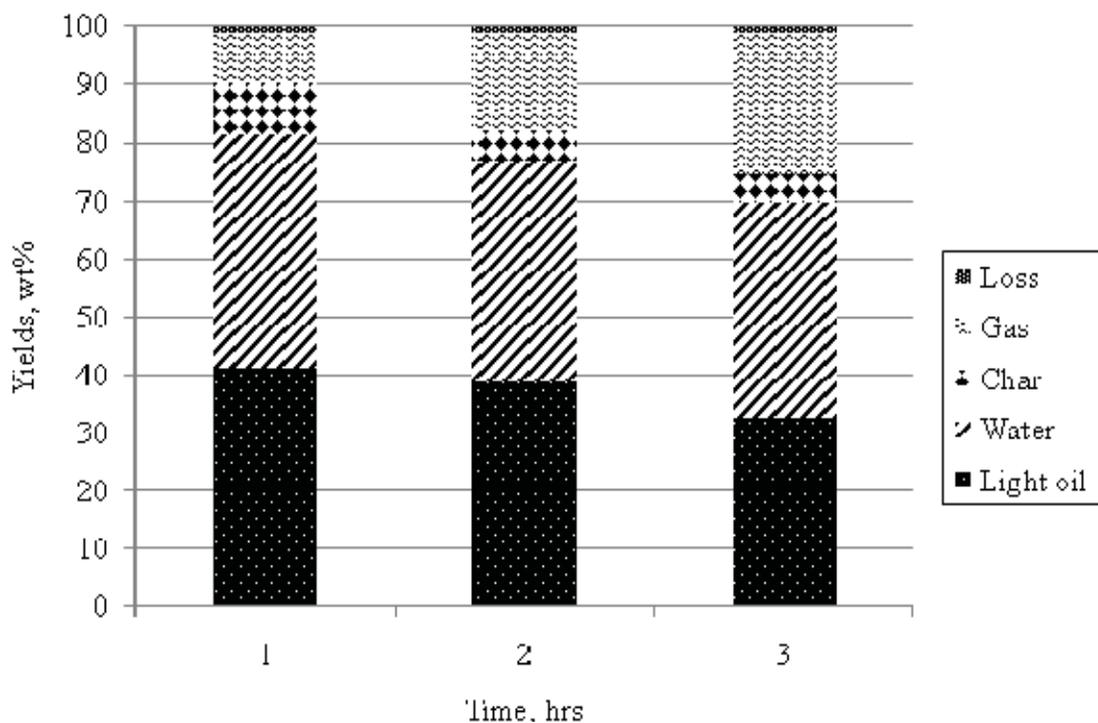
Figure 3.1   Mass balances from the HC reaction produced by MSU-2, CoMo/Al and
NiMo/Al at temperature of 400 $^{\circ}$C, pressure of 1500 psig for a reaction
time of 2 h.

The aqueous fractions formed by the catalytic HC reactions were nearly equal,

ranging from 10-11.1 wt%. Char yields ranged from approximately 3.5 to 7.2 wt%. The

highest char yields were for NiMo/Al at 7.2 and 6 wt% for CoMo/Al. The high char yield

for these catalysts is considered to be due to the high acidity of the gamma-alumina

support. It is well known that the acidity of an alumina support forms a high amount of

char [4, 22]. Lowest char is observed with MSU-2 catalyst, this may be considered as

selective hydrocracking nature of the catalyst. Undoubtedly, some of the increased liquid

yield provided by MSU-2 resulted from reduced conversion of HT organic liquid to char.

The respective gas yields from the HC reactions were 3.5, 6.0 and 7.2 wt% for MSU-2,

CoMo/Al and NiMo/Al. MSU-2 had the lowest gas yield.

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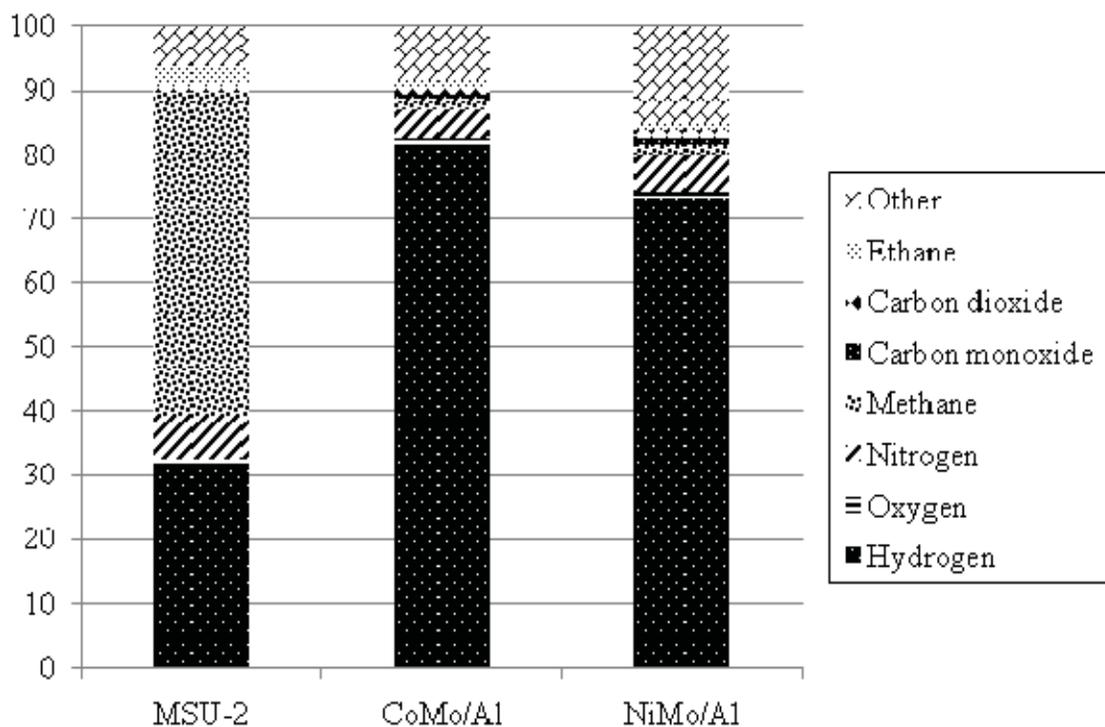
Figure 3.2   Gas compositions of the gases collected after the second-stage HDO of mild HDO bio-oil with different catalysts (400 ^{o}C, 1500 psig, and 2 h).

Figure 3.2 identifies and quantifies the gas phase components produced by the MSU-2, NiMo/Al and CoMo/Al HC reactions. The major gas component produced by CoMo/Al and NiMo/Al was un-reacted hydrogen with respective percentages of 81.6 and 73.2 wt%. Surprisingly, the major gas component produced in the MSU-2 HC reaction was methane gas rather than unreacted hydrogen. The respective percentages of methane gas produced by MSU-2 were 50.2 wt% with the unreacted hydrogen gas component comprising 31.4 wt%. A possible pathway for the methane formation was due to a methanation reaction initiated by the MSU-2 catalyst in the presence of hydrogen with the char carbon at a temperature above 350 ^{o}C [13, 22]. Methane produced by MSU-2 catalyst with the expense of hydrogen gas when compared with NiMo/Al and CoMo/Al is very high and consumes more hydrogen, this is undesirable in terms of pilot scale and it is eventually increase the capital cost of the HT process, but on the same lines MSU-2

catalyst did not need any presulfidation prior to its usage and also producing zero hydrocarbon with marginally high yields compared to CoMo/Al and NiMo/Al. These advantages may possible overcome the high hydrogen consumption and also maintain the process overall cost effective. Further research should be conducted to minimize the methane formation by MSU-2 catalyst by performing experiments at reduced level of hydrogen pressure.

The product hydrocarbon yield and oxygen content (determined by elemental analysis) of the oil phase are taken as a measure of catalyst performance. Figure 3.3 shows oxygen content on y-axis as a function of yield on the x-axis for each catalyst tested. The total organic product yields for all seven catalysts varied between 66 and 68 wt%. The highest hydrocarbon oil yield was obtained for MSU-1(68 wt%) and followed by NiMo/Al (66.5 wt%) and CoMo/Al (66 wt%). The oxygen content of the organic liquid product for all the three catalysts varied between 0.01-3 wt%. Highest oxygen content was observed for CoMo/Al while the lowest was for MSU-2. It is not surprising that CoMo/Al had high oxygen content. As previously noted CoMo/Al produces oil that is not fully hydrotreated and would, therefore, be expected to have unreacted oxygenates. The high deoxygenation level of MSU-2 corresponds to its dual functional nature of the catalyst i.e. High hydrocracking activity of oxygenates and isomerization activity to form hydrocarbons.
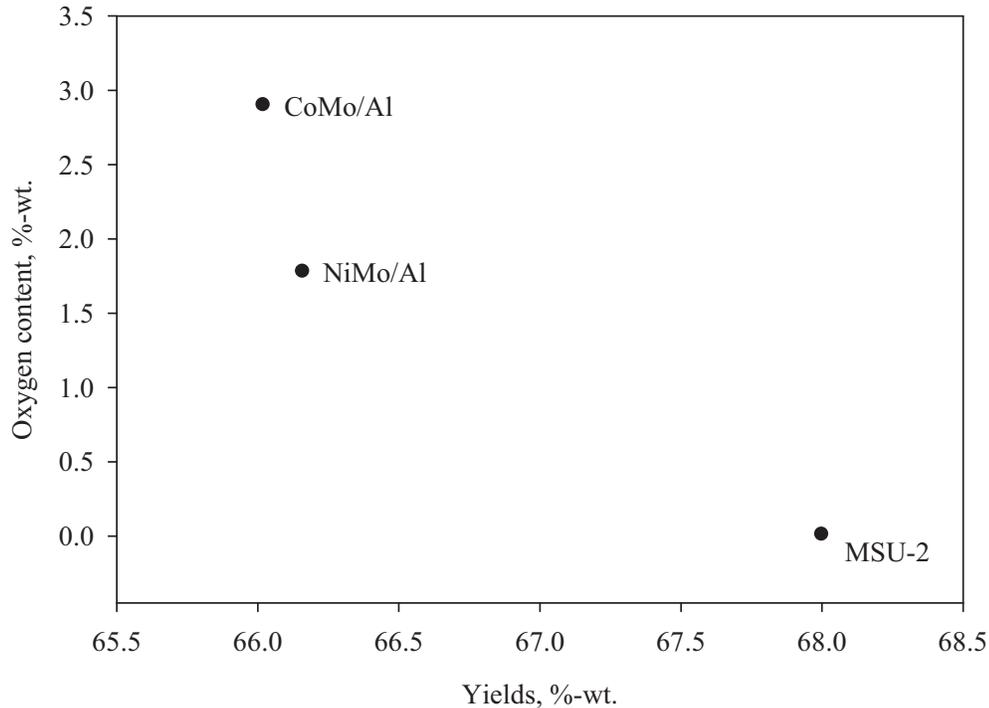
Figure 3.3   Product oil yields and oxygen contents produced by the study catalysts
              following HC catalysis.

Van Krevelen plots of molar H/C-O/C are the best method for the evaluation of

quality of the product oils and hydrocracking activity of the screened catalysts. For

comparison molar H/C and O/C ratios of raw bio-oil and diesel fuel are also provided in

Figure 3.4 to compare with hydrotreated oils. Higher hydrogenation activity corresponds

to higher H/C ratio and lower O/C ratio. In Figure 3.3, three distinct areas are visible 1)

raw bio-oil, 2) CoMo/Al, NiMo/Al and HT organic liquid and 3) MSU-2 and diesel fuel.

The raw bio-oil has higher O/C ratio, this is due to the presence of higher percentage of

oxygen content in the form of oxygenated compounds. Thus, the raw bio-oil is different

from the hydrotreated upgraded oils. In the upgraded oils MSU-2 catalyst is exhibiting

higher H/C ratio among all the catalyst tested and almost similar O/C ratio with the diesel

fuel. This implies MSU-2 catalyst is showing higher hydrocracking activity than the other two catalysts.
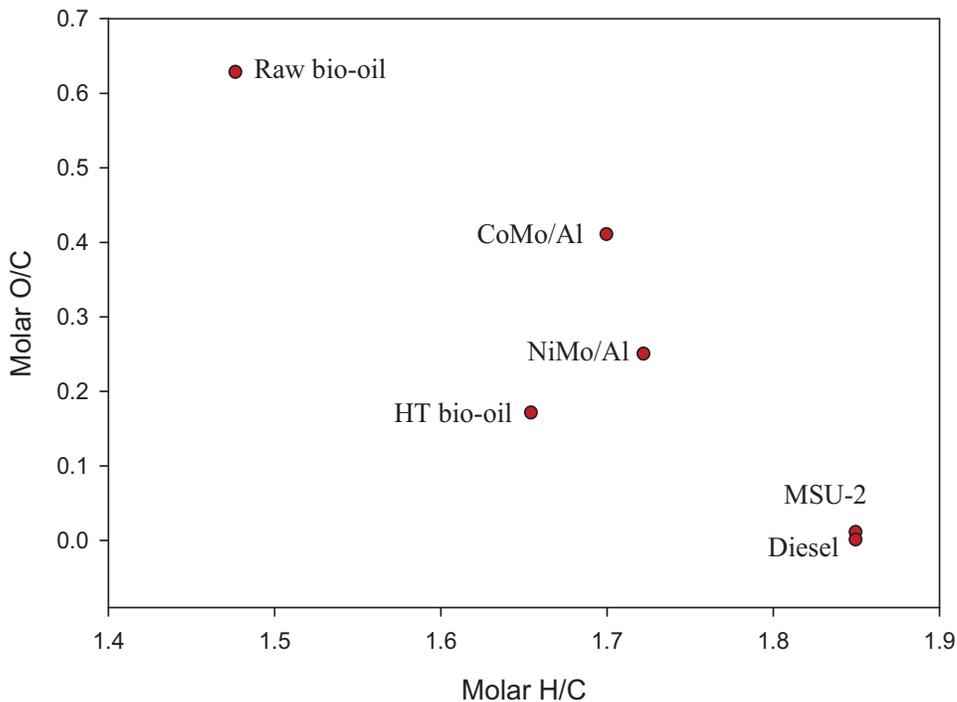
Figure 3.4   Van Krevelen plots of molar H/C-O/C (elemental composition) of the product oil obtained from HC of HT organic liquid.

An analysis of variance (ANOVA) was performed on the hydrocarbon product yield results of the screened catalysts by catalyst type. The ANOVA was highly significant at the   0.003 level allowing comparisons of means by Fisher's protected LSD method. Figure 3.5 provides a graph comparing the hydrocarbon product oil yield values and results of a comparison of means test of these values, for each catalyst. These results show that MSU-2 had the significantly highest yield at 68.5 wt%. Likewise, Ni Mo/Al and CoMo/Al did not differ significantly with respective yields of 66.5.1and 66

wt%. The statistical analysis of yield results shows That MSU-2 produced higher yields above the 2 other tested catalysts.
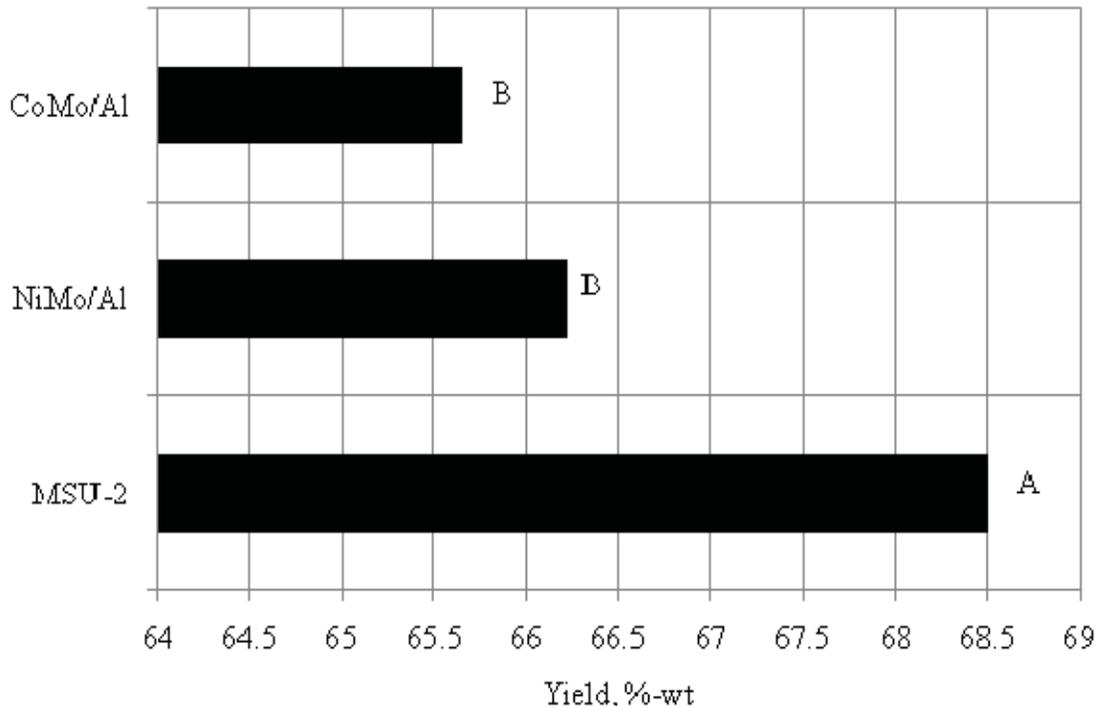
Figure 3.5   Comparison of means results for hydrocarbon product yield values for MSU-2, CoMo/Al and NiMo/Al catalysts. Different letters at end of histogram indicate the noted means differed.

An analysis of variance (ANOVA) was performed on the char and water yield results of the screened catalysts by catalyst type. The ANOVA was highly significant at the 0.001 level for char yields and significant at the 0.0191 level for water yields allowing comparisons of means by Fisher's protected LSD method. Figure 3.6 provides a graph comparing the char and water yield values and results of a comparison of means test of these values, for each catalyst. These results show that MSU-2 had the significantly lowest char yield of 3.5 wt%. Likewise, Ni Mo/Al and CoMo/Al differ significantly with respective char yields of 7.3 and 6.2 wt%. The statistical analysis of

water yield results shows That MSU-2 produced lower char yields above the 2 other

tested catalysts. For water yields results show that, MSU-2 had the significantly lowest

water yield at 9.9 wt%. Likewise, Ni Mo/Al and CoMo/Al did not differ significantly

with respective water yields of 11.53 and 11.29 wt%. The statistical analysis of yield

results shows that MSU-2 produced lower water yields than did the two other tested
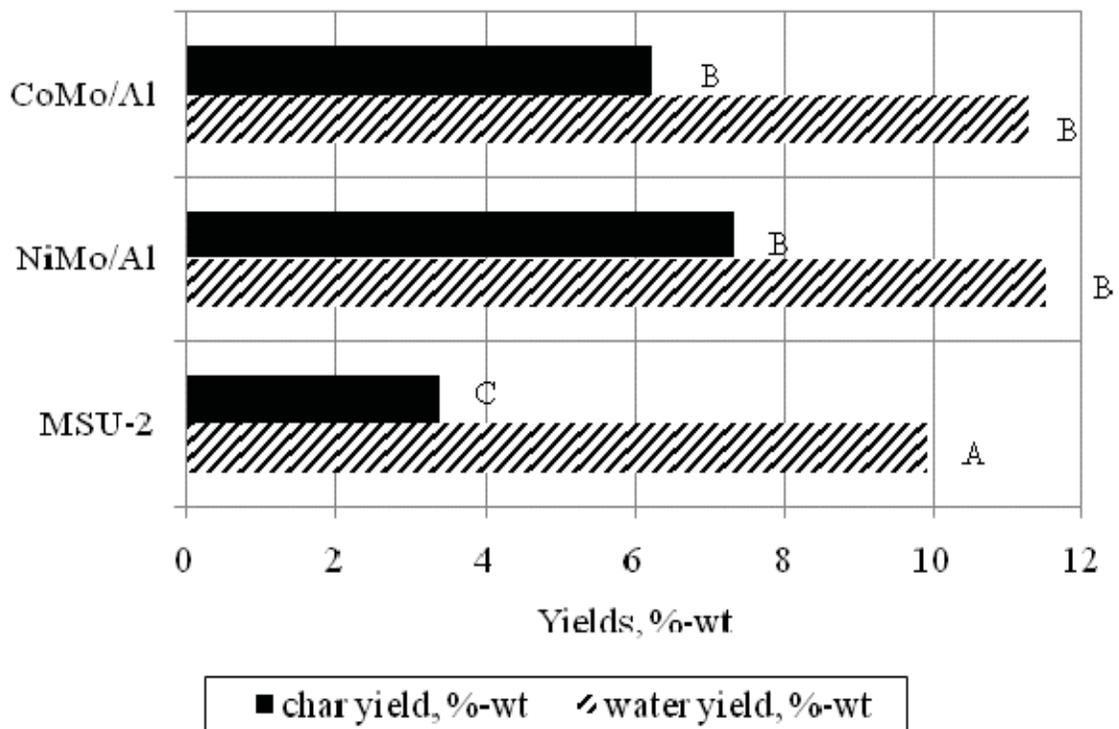
catalysts.

Figure 3.6   Comparison of   means results for char and water produced during the HC
             catalysis of the HT organic fraction for r MSU-2, CoMo/Al and NiMo/Al
             by ANOVA data analysis. Different letters at end of histogram indicate the
             noted means differed.

An analysis of variance (ANOVA) was performed on the oxygen content of the

hydrocarbon product results of the screened catalysts. The ANOVA was highly

significant at the 0.003 level allowing comparisons of means by Fisher's protected LSD

method. Figure 3.7 provides a graph comparing the oxygen content of the hydrocarbon

product values and results of a comparison of means test of these values, for each

catalyst. These results show that MSU-2 had the significantly lowest oxygen content of

0.01 wt%. Ni Mo/Al and CoMo/Al were significantly different from each other with

respective oxygen contents of 1.96.1and 2.8 wt%. The statistical analysis of yield results

shows that MSU-2 produced lowest oxygen content hydrocarbon product above the two

other tested catalysts.
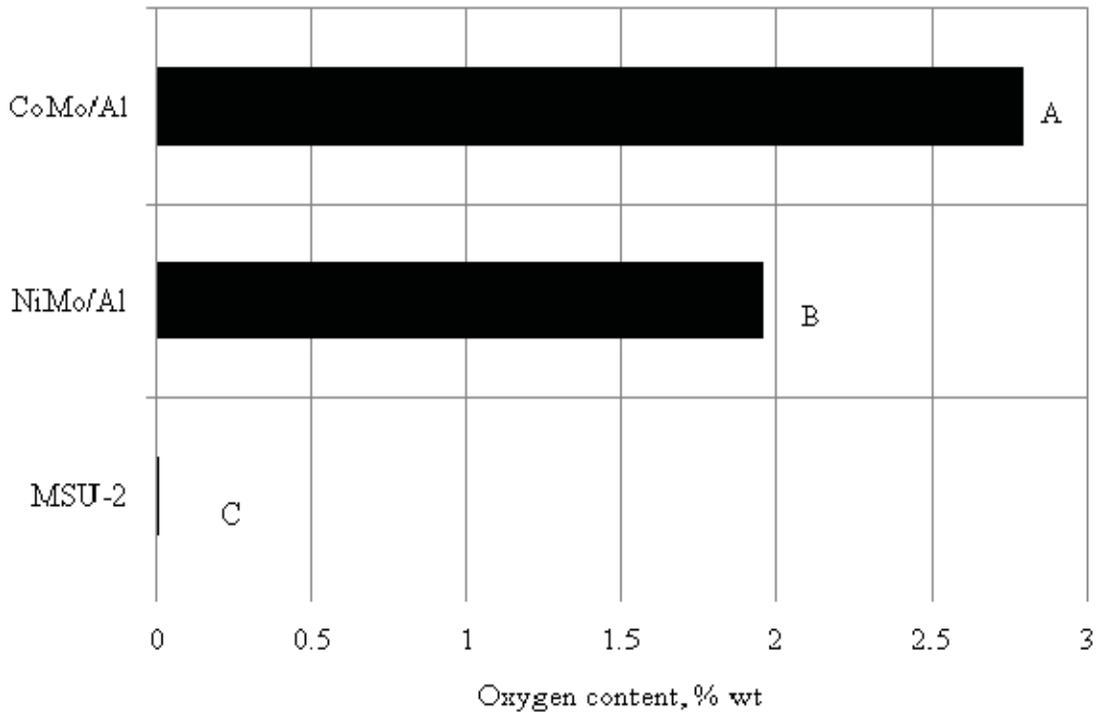
Figure 3.7   Comparison of oxygen content of the hydrocarbon product yield values for
MSU-2, CoMo/Al and NiMo/Al by ANOVA data analysis. Different letters
at end of histogram indicate the noted means differed.

The results of the statistical analysis of hydrocarbon product yield, char yield,

water yield and oxygen content indicate that the MSU-2 catalyst had significantly better

results in terms of all the treatments. CoMo/Al and NiMo/Al have significantly highest

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yields ratio with highest char yields but in terms of oxygen content they ranked significantly the lowest. However, methane produced by MSU-2 catalyst at the expense of unreacted hydrogen gas is problematic when compared with NiMo/Al and CoMo/Al results. This unreacted gas would be captured and reused for hydroprocessing in an industrial system and thereby, lower the hydrogen cost for hydroprocessing. However, the objective of this project is the production of zero oxygen content combined with adequate yield of liquid product. In these terms the MSU-2 catalyst performed the best. Therefore, the MSU-2 catalyst was selected as the catalyst with which to perform subsequent temperature and reaction time experiments.

Table 3.4   Physical and chemical properties of hydrocarbon mix from hydrocracking HT organic liquid with MSU-2, NiMo/Al and CoMo/Al catalysts.

Property	MSU-2	CoMo/Al	NiMo/Al
Acid value, mg KOH/g	0.01	0.28	0.28
Water content, wt%.	0	0	0
HHV, MJ/kg	45.53	43.85	43.77
Density, g/mL	0.82	0.84	0.83

Table 3.4 summarizes the physical and chemical properties HC hydrocarbon mix of HT organic liquid using MSU-2, NiMo/Al and CoMo/Al catalysts. From Table 3.4, it is observed that MSU-3 has the lowest acid value of 0.01 among the other two catalysts; water content is zero for all the samples; HHV is highest for MSU-1. From Table 3.4, it is obvious that, MSU-2 catalyst is a superior hydrocracking catalyst among all the catalysts tested.

3.4.2 HC process optimization

3.4.2.1 Effect of reaction time for HC process with MSU-2 catalyst

Experiments were performed with MSU-2 catalyst selected from screening studies at various reaction times ranging from 1 to 4 h with 1h intervals. The relative amounts of the water, oil, solids and gas phases were determined experimentally, for the overall mass balance of the process. For all the experiments best mass balance closures between 97-99 wt% are observed. The product oil yield and oxygen content (determined by elemental analysis) of the oil phase are taken as a measure of catalyst performance. The oxygen content of the organic phase as a function catalytic activity is given in Table 3.5, where the oxygen content of the product oil is compared versus the oil yields from the different reaction times. From Table 3.5, the total product oil yield varies between 60 and 72 wt%. The highest oil yields were obtained for 1 h and lowest for 4. The oxygen content of the oils varies between 0.00 and 1.19 wt%. It clear from the Table 3.5, as the reaction time increases product oil yield decreases and subsequently oxygen content of the product also decreases [23]. To achieve highest oil yields without compromising the oxygen content, 2 h reaction time is sufficient for the removal of all the oxygen to produce a hydrocarbon mix product.

Table 3.5   Effect of reaction time on product yields and oxygen content of the product oils obtained by HC with MSU-2 catalyst.

Time, h	Yield, wt%	Oxygen content, wt%
1	72.4	1.19
2	68.1	<0.5
3	62.4	0.0
4	60.3	0.0

3.4.3 Calculation of hydrogen consumption and energy efficiency of the HC process

Hydrogen consumption could not be calculated accurately in the high pressure batch autoclave set-up. However, for all the experiments mass balances, gas phase compositions and elemental analysis are determined experimentally and therefore use it for calculation of hydrogen consumption. Calculations are performed for the HC of stabilized bio-oil with MSU-2 catalyst at 400 $^\circ$C for 2 h. On the basis of equation 3.1, theoretical hydrogen consumption for the HC process is 177Nl/kg dry bio-oil. Actual hydrogen consumption is calculated as 232 Nl/kg dry bio-oil. This value is 24% higher than the theoretical value calculated and it is explained as, the formation of methane gas in the reaction with the expense of hydrogen gas. The hydrogen consumption in HC process with MSU-1 is 50% lower than the previously reported literature [4, 13, 22]. Detailed calculation of the hydrogen consumption of HC process is presented in Appendix B (B.1).

A simplified schematic HDO chemical reaction is shown in Eq. 3.1 below.

$$\text{-(CHO)-} + H_2 \longrightarrow \text{-(CH)-} + (H_2O, CO_2, CH_4, CO) \qquad \text{(Eq. 3.1)}$$

Energy efficiency of the HC process is calculated using the following equation 3.2 [24]

$$Energy\ efficiency = X_{HC.} \frac{HHV_{product}}{HHV_{HT\ organic\ liquid}} .100\% \qquad \text{(Eq.3.2)}$$

Where,

X_{HC}: HC product oil yield = 68.1 wt% of total product

$HHV_{product}$: Heating value of HC product oil = 45.53MJ/kg

$HHV_{HT\ organic\ liquid}$: Heating value of HT organic liquid = 33.12 MJ/kg

Using the above equation, the calculated energy efficiency is 93.6%. This value is 35 to 40% higher than the previously reported literature and also it is 10% higher than the commerical hydotreating catalysts such as CoMo/Al and NiMo/Al[24].

3.5   Product analysis

3.5.1   Physical and chemical properties

Table 3.8 summarizes the physical and chemical properties of raw bio-oil, HT organic liquid, and HC hydrocarbon mix with diesel fuel. The raw bio-oil contained acid value of 95; density of 1.2 g/mL; oxygen of 43.5 wt%; water content of 23.5 wt%; viscosity was 10.15 cSt with. Bio-oil pH was 2.3 and acid value was 95. Bio-oil HHV measured was 17 MJ/kg. The first-stage HT organic liquid has acid value of 58; pH was 4.10; density of 0.95 g/mL; water content of 5 wt%; oxygen content of 19.5 wt%; and HHV of 33.12 MJ/kg.

The hydrocracked product produced from the application of second-stage HC of HT organic liquid was water clear hydrocarbon mix shown in Figure 3.8. A minor amount of char residue, considered to be uncatalyzed carbon, was contained in this product but was easily removed by brief centrifugation. The properties of the final hydrocracked product had undetectable oxygen content; viscosity decreased to 2.6, very close to that of petroleum diesel; Density was 0.77 g/mL, about midway between the values for petroleum gasoline and diesel. pH of the hydrocarbon was a nearly-neutral 6.5 which is confirmed by the very low total acid number of less than 0.1. HC hydrocarbon mix has very high HHV of 45.4 MJ/kg, which is similar to diesel fuel HHV (45.65 MJ/kg).

The zero oxygen content and low acid value are unique results among those reported by practitioners of bio-oil hydroprocessing [4]. Also, HC hydrocarbon mix has almost similar energy content with respect to petroleum fuels. This is the result of the effectiveness of the MSU-2 catalyst. Zero oxygen content will allow the hydrocarbons produced by the MSU-2 catalyst to be introduced into petroleum refineries directly ahead of the distillation process.

Table 3.6   Physical and chemical properties of raw bio-oil, HT organic liquid and HC hydrocarbon mix compared with diesel fuel.

Property	Raw bio-oil	HT organic liquid	HC bio-oil	Diesel[a]
Oxygen (wt%)	43.5	19.55	<0.1	0
Viscosity (cSt) at $40\,^{\circ}C$	10.15	7.80	2.65	2.60
Density (g/mL)	1.20	0.95	0.79	0.83
pH	2.30	4.10	6-6.5	6-6.5
Acid value (mg KOH/g)	95.00	58.00	~0.1	0
Water content (wt%)	23.50	5.00	0.0	0
HHV (MJ/Kg)	17.10	33.12	45.40	45.65

Figure 3.8   Water clear hydrocarbon mix produced by HC process using MSU-2 catalyst.

3.5.2   Detailed hydrocarbon analysis (DHA)

Petroleum fuels such as gasoline, diesel and jet fuel are complex mixtures of hundreds of compounds. Information about concentrations of the individual components is important for evaluating raw materials and controlling refinery processes. A high-resolution GC method for DHA of these fuels is outlined in American Society of Testing and Materials (ASTM) Method D-6730-01 often referred to as the PONA (paraffins, olefins, naphthenes, and aromatics) or PIANO (paraffins, *iso*-paraffins, aromatics, naphthenes, and olefins) analysis [4]. ASTM D-6730-01 is specific for the analysis of these hydrocarbon components, plus oxygenated additives such as methanol, ethanol, tert-butanol, methyl tert-butyl ether (MTBE), and tert-amyl methyl ether (TAME) in spark-ignition engine fuels.
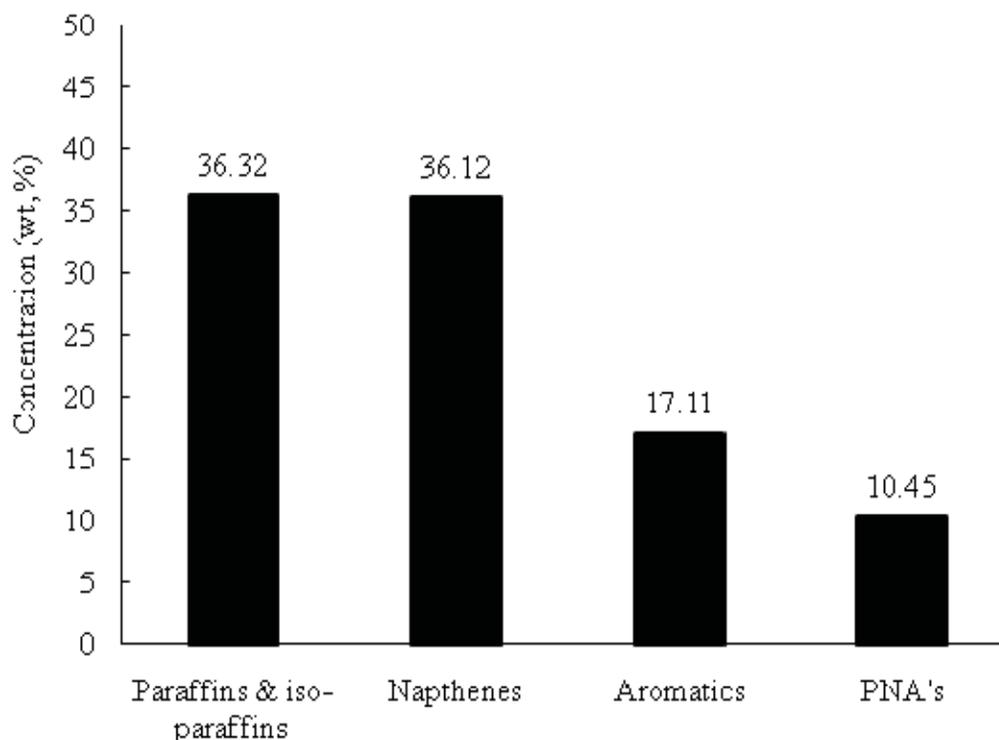
Figure 3.9   DHA of HC hydrocarbon mix grouped by hydrocarbon type.

A sample of 50 mL HC hydrocarbon was sent to INTERTEK LAB in Houston for

testing of ASTM D6730-01. Figure 3.9 summarizes the ASTM D6730-01 DHA report of

the hydrocarbon mix produced by the HC hydrocracking treatment. Complete report on

DHA analysis can be seen in Appendix B (Table B.1). The DHA provided a list of all

hydrocarbons types contained in the hydrocarbon mix and was comprised of greater than

300 compounds. All these compounds are categorized by their respective type and

grouped as follows paraffins and iso-paraffins (37%), napthenes (36%), aromatics (17%)

and polynucleararomatics (PNAs) (11%). Paraffins and iso-paraffins are likely to be

formed by the severe hydrocracking of low molecular weight compounds present in HT

organic liquid. Napthenes and aromatics are compounds formed by the hydrogenation

followed by hydrocracking of phenols and substituted phenols [4, 24]. PNA's are likely

formed due to the occurrence of polymerization reactions with respect to aromatic compounds formed during the course of reaction [4, 24].

Zero olefins and no oxygenated compounds were identified among the 300 compounds characterized by the DHA. Table 3.9 gives a subset of the 300 hydrocarbon compounds initially identified in the HC hydrocarbon mix by DHA. The subset was developed by grouping similar hydrocarbons into larger groups. The subset of HDO bio-oil hydrocarbon compounds identifies wide range hydrocarbons with carbon numbers ranging from C-4 to C-20. High concentrations of alkanes, cycloalkanes and aromatic hydrocarbons and their derivatives are identified. No oxygenated compounds are represented among the compounds detected. Heavier hydrocarbons, ranging in carbon number above C-20 are present in only miniscule quantities. It is clear from this characterization that gasoline (C4-C10), diesel (C10-C16) and jet fuel (C4-C12) hydrocarbon types comprise this hydrocracked product.

Table 3.7   Subset of 300 hydrocarbon compounds initially identified by detailed hydrocarbon analysis of HC hydrocarbon mix.

Compound name	Concentration (wt%)	Compound name	Concentration (wt%)
propane	0.141	methyl ethyl cyclopentane	0.086
isobutane	0.071	cis-1-ethyl-2-methylcyclopentane	0.112
butane	0.932	C8-Naphthene	0.007
isopentane	0.524	cis-1,2-dimethylcyclohexane	0.215
pentane	1.934	ethylcyclohexane	5.118
cyclopentane	1.555	1,1,3-trimethylcyclohexane	0.027
isohexane (2-methylpentane)	0.367	3,5-dimethylheptane	0.054
3-methylpentane	0.366	c-1-ethyl-4-methylcyclohexane	0.031
hexane	1.974	c-1-ethyl-2-methylcyclohexane	0.045
methylcyclopentane	2.658	t-1ethyl-4-methylcyclohexane	0.04
benzene	0.892	Ethylbenzene	1.396

Table 3.7 (continued)

cyclohexane	3.777	trimethyl cylco hexanes	0.128
2-methylhexane	0.238	*p*-Xylene	0.745
2,3-dimethylpentane	0.058	*m*-Xylene	0.280
1,1-dimethylcyclopentane	0.035	*o*-xylene	0.407
3-methylhexane	0.423	C9-aliphatics	7.915
trans-1,3-dimethylcyclopentane	0.353	1-methyl-c-4-ethylcyclohexane	0.603
cis-1,3-dimethylcyclopentane	0.314	butylcyclopentane	0.585
trans-1,2-dimethylcyclopentane	0.252	n-propylbenzene	1.648
heptane	1.134	1-methyl-3-ethylbenzene	0.587
methylcyclohexane	6.200	1-methyl-2-ethylbenzene	0.326
1,1,3-trimethylpentane	0.025	mix C10's(arom-Naphthenes*iso-paraffins)	4.283
ethylcyclopentane	1.252	N-C10	0.292
dimethylhexane	0.026	Indane	0.382
1,2,4-trimethylcyclopentane	0.131	n-butylcyclohexane	0.635
toluene	2.189	mix C11's(arom-Naphthenes*iso-paraffins)	6.686
2,3-dimethylhexane	0.030	penyl cyclo hexane	0.913
1,1,2-trimethylcyclopentane	0.026	tetra hydro Naphthalene	1.371
2-methylheptane	0.152	Naphthalene	0.146
4-methylheptane	0.112	multi hydro PNA's	9.229
trans-1,3-dimethyl cyclohexane	0.019	dicyclohxylmethane	0.452
3-methylheptane	0.249	N-C15	0.154
dimethylhexane	0.084	multi hydro PNA's & cyclics(C11-16)	3.747
cis-1,3-dimethylcyclohexane	0.557	n-C16	1.740
trans-1,4-dimethylcyclohexane	0.169	1-phenyl-2-cyclohexylethane	0.558
dimethylhexane	0.036	mix hydrocarobons(C17-C18)	6.845
trans-1-ethyl-3-methylcyclopentane	0.583	n-C17	2.675
1-ethyl-2-methylcyclopentane	0.272	heavier hydrocarbons(C18-C20)	2.423
trans-1,3-dimethylcyclohexane	0.239	octadecane	0.394
octane	0.855	heavier hydrocarbons(C18-C20)	5.054
cis-1,3-dimethylcyclohexane	0.464	**Total**	**100**

3.5.3 FTIR analysis of HT organic liquid, HC hydrocarbon mix and diesel fuel

FTIR spectroscopy is proven to be a very versatile technique for identification of organic functional groups in the bio-oil and HDO product oil. Figure 3.10 shows the comparison of FTIR spectra representing functional group compositional analysis from, HT organic liquid, HC hydrocarbon mix and petroleum diesel. There is a significant

difference observed between HT organic liquid and HC bio-oil. In HT organic liquid the broad absorbance band between 3050 and 3600 cm^{-1} are ascribed to γ(O–H) vibrations of hydroxyl groups which indicate the presence of alcohols, phenols and water in the raw bio-oil. In the case of HC hydrocarbon mix this peak is not visible; this confirms the reduction of phenolic and alcoholic groups to hydrocarbons.

In HT organic liquid the presence of OH absorbance peak together with the presence of C=O stretching vibrations between 1650 and 1750 cm^{-1} indicates the presence of carboxylic acids ketones, quinines, aldehyde groups and their derivatives, but these peaks are also not seen in HC hydrocarbon mix spectrum, which is also confirmed by the acid value estimation (0.1) of HC oil in Table 3.8. 3000-2800 cm^{-1} and 1500-1400 cm^{-1} sharp peak confirms the presence of alkanes in HC hydrocarbon mix. A sharp peak at C-H stretching 2937 cm^{-1} together with band at 724 cm^{-1} confirms the presence of aromatics, substituted aromatics and PNA's which is similar to petroleum diesel and this is a significant increase compared with HT organic liquid. The presences of alkanes and aromatics compounds are also confirmed by detection of aliphatic hydrocarbons and aromatics in HC hydrocarbon mix by DHA.
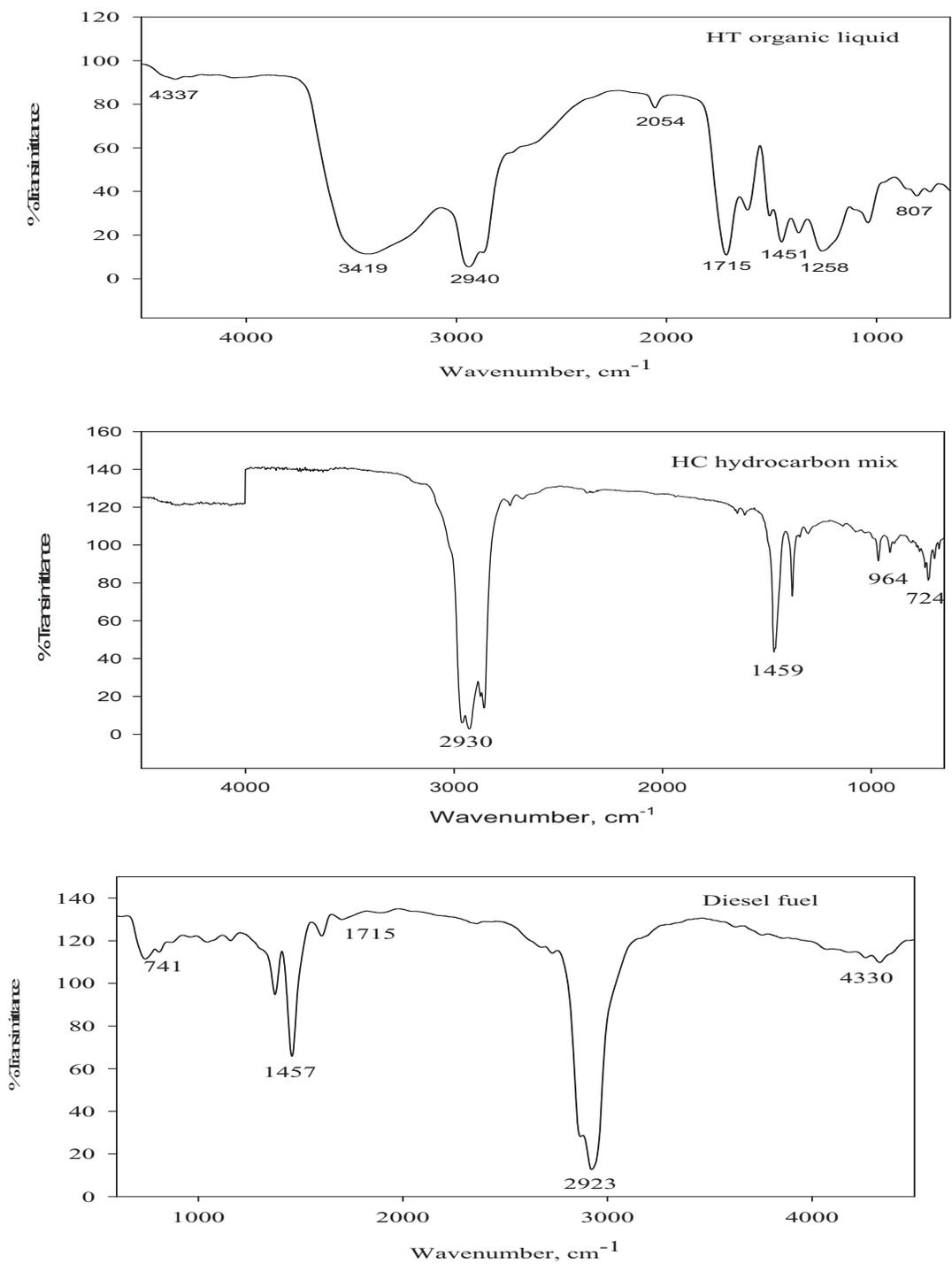
Figure 3.10   FTIR spectral comparisons of (a) HT organic liquid (b) HC hydrocarbon mix and (c) diesel fuel.

3.5.4 NMR analysis of HT organic liquid, HC hydrocarbon mix and diesel fuel

Typical ^{1}H-NMR spectra of HC hydrocarbon mix, compared with HT organic liquid and diesel fuel are given in Figure 3.11. The HC hydrocarbon mix spectrum is a very complex and consists of large number of signals due to the presence of different hydrocarbon types and molecular structures. Certain regions particularly 0.4-2.0 ppm, are highly overlapped and not well resolved. Aliphatic hydrocarbons are generally situated in this region.

From Figures 3.12 (a) and (b), there is a significant difference between ^{1}H-NMR spectrum of HT organic liquid and HC hydrocarbon mix. The major difference identified is detection of saturated aliphatic protons with increased intensity in the range between 0.0 to 2.5 ppm in HC hydrocarbon mix; this is also confirmed by DHA analysis. The 0-2.5 ppm region is almost similar to the 0-2.5 ppm region present in diesel fuel spectrum. Another major difference observed in HC hydrocarbon mix is a strong reduction in the peak intensity between 3 to 8 ppm when compared with HT organic liquid spectrum. This suggests that phenol and phenolic derivates are reduced to a significant amount in HC hydrocarbon mix with MSU-2 catalyst. In addition, HC hydrocarbon mix has aromatic protons in the range of 6 to 8 ppm are also detected similar to diesel fuel spectrum.

From the ^{1}H-NMR analysis, it is clearly evident that the HC hydrocarbon mix is significantly different from HT organic liquid and also it has close resemblance with the petroleum diesel fuel.
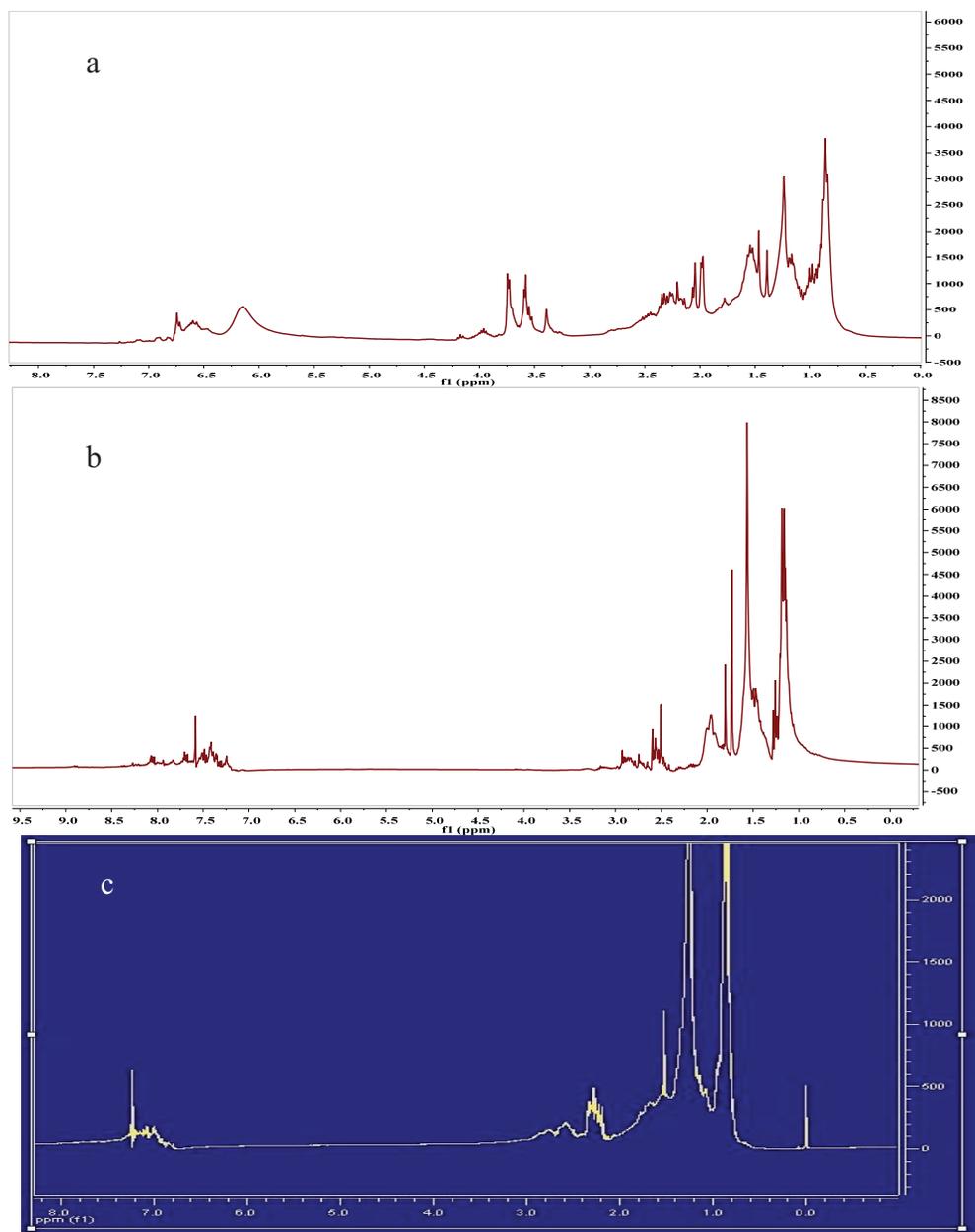
Figure 3.11 ^{1}H- NMR spectra of (a) HT organic liquid (b) HC hydrocarbon mix (c) diesel fuel (Bruker 300 MHz, CDCl$_3$ as solvent).

3.6   ASTM D2887/D6352 Simulation distillation plot

Simulated distillation results are shown in Figure 3.12 to compare the vapor boiling points of petroleum gasoline, jet fuel and diesel fuels to the HC hydrocarbon mix. From Figure 3.13, it is observed that the HC hydrocarbon mix has a vaporization

temperature profile that is an approximate weighted mean of petroleum gasoline and diesel fuels. Precisely it falls in between gasoline and jet fuel range.
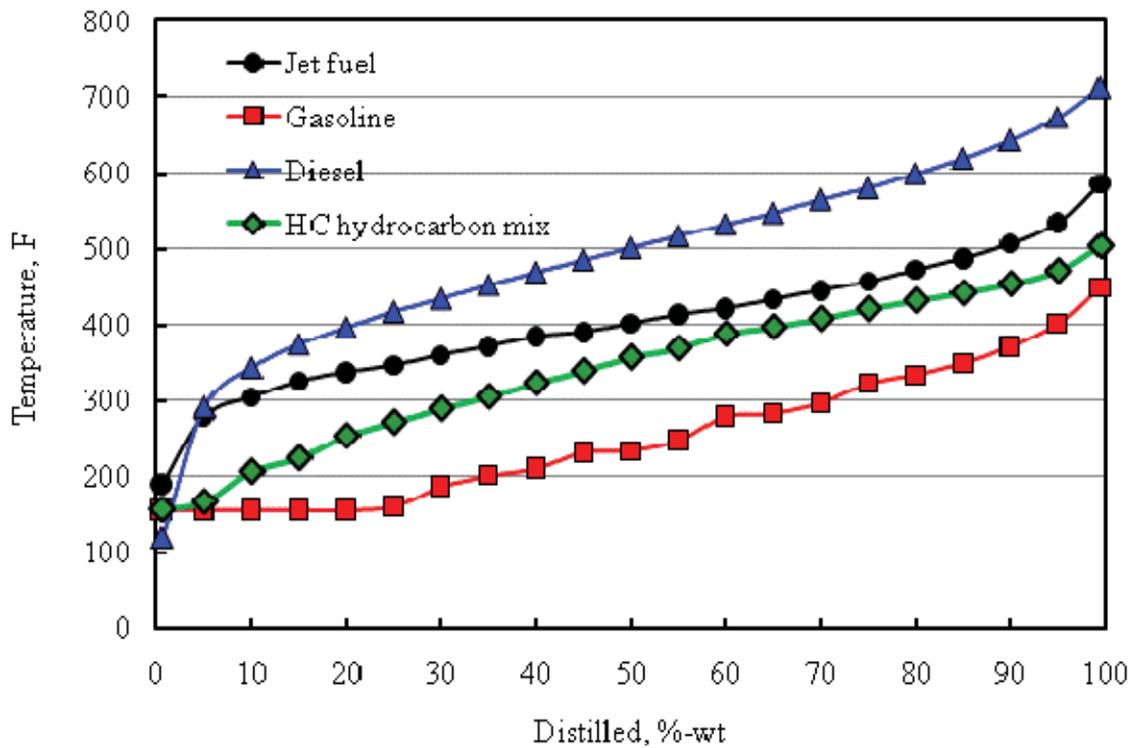
Figure 3.12   Simulated distillation study of HC with gasoline, jet fuel and diesel fuels.

From this observation it is believed that HC hydrocarbon mix has a variety of hydrocarbons present. Estimate of these various hydrocarbon of different fuel types are presented in Figure 3.13. Figure 3.13 shows the approximate distribution of these by fuel weights and results in as gasoline comprising 37%, jet fuel 27%, diesel 25% and heavy fuel oil 11%. From these simulation studies, it is concluded that HC hydrocarbon mix contains various fuel types. Thus, the next step is to separate the hydrocarbon mix into various fuel types depending on their boiling range temperatures. Fractional distillation technique is used to separate the hydrocarbons into different fuel types.
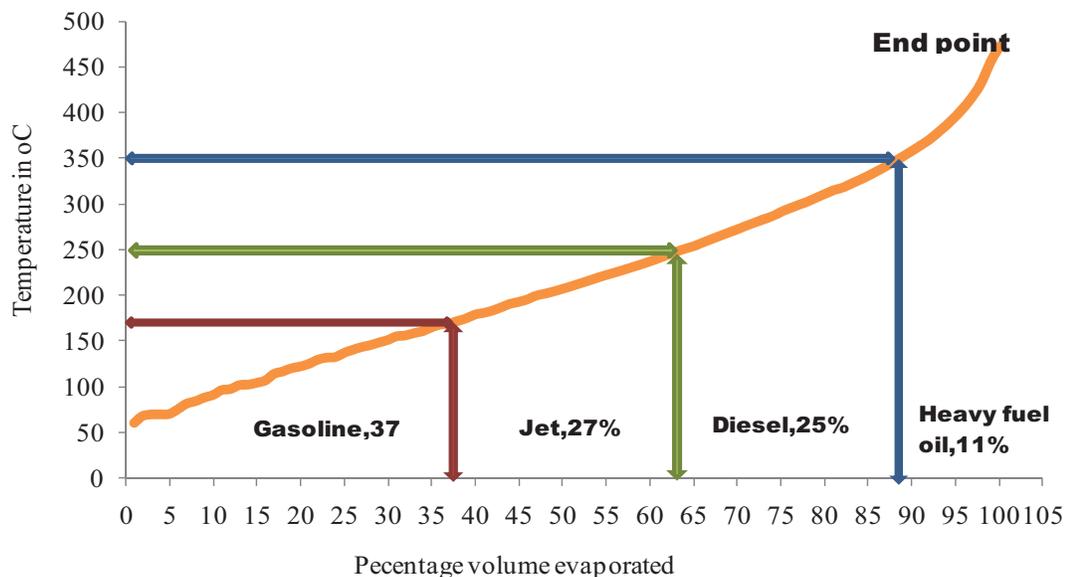
Figure 3.13   Simulated distillation curve of HC hydrocarbon mix for boiling range distribution of petroleum fractions by gas chromatography (ASTM D2887).

3.7   Fractional distillation study of HC hydrocarbon mix in to various fuel types

Fractional distillation is a separation technique used to separate the component parts or fractions present in a mixture, such as separating chemical compounds based on their boiling points by heating them to specific temperature at which the compounds evaporate [25]. A typical HC hydrocarbon mix prepared using MSU-2 catalyst, was subjected to a fractionation procedure to obtain products with an increased hydrocarbon nature, and as such more resemblance to the transportation fuels. Fractional distillation is performed by using spinning band distillation apparatus as shown Figure 3.14(a). Results from the fractional distillation study of HC bio-oil are presented in Figure 3.14(b).

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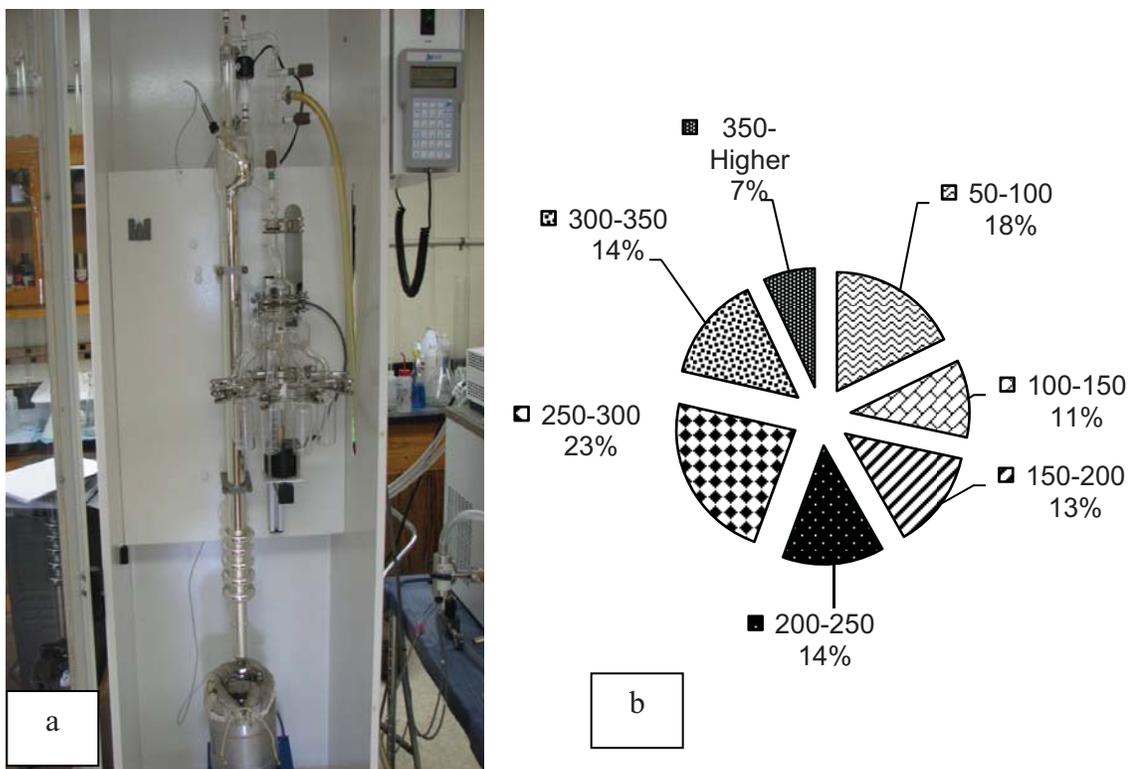
Figure 3.14   (a) Spinning band distillation apparatus (b) percentage of fractions obtained after fractional distillation of HC bio-oil.

A total of seven different fractions were obtained at different boiling point ranges between 50 to greater than 350°C. The yields of the fractionated products with respect to their boiling point range are given as follows 50-100 ^{o}C yields 18 wt%; 100-150 ^{o}C yields 11 wt%; 150-200 ^{o}C yields13 wt%; 200-250 ^{o}C yields 14 wt%; 250-300 ^{o}C yields 23 wt%; 300-350 ^{o}C yields 14 wt% and finally temperature greater than 350 ^{o}C yields 7 wt% of fractionated product.

In a typical petroleum refinery, fractional distillation of crude oil uses the same principle as above and results in various fractions at different boiling point ranges i.e. gasoline fraction between 0-170 ^{o}C ; jet fuel fraction between 170-250 ^{o}C ; diesel fraction between 250-350 ^{o}C and heavy fuel oil at 350 ^{o}C and higher temperatures.

Out of seven fractions collected from fractional distillation of hydrocarbon mix, two fractions were selected (100-150 and 200-250 ^{o}C) and subjected to perform simulated distillation and subsequently compared with regular petroleum gasoline and jet fuel (Jet A). These two fractions 100-150 and 200-250 ^{o}C are selected to identify the possible similarities of hydrocarbon mix with gasoline (70-170 ^{o}C) and jet fuel (170-250 ^{o}C).

Simulated distillation curves of selected fractions, gasoline and jet fuel are presented in Figure 3.15. It is clear from Figure 3.15 that, 100-150 ^{o}C is almost coincides with the gasoline fractions and it is also similar in case of 200-250 ^{o}C fraction with respect to jet fuel. For further identification, FTIR spectra of the two selected fractions, gasoline and jet fuel are recorded and presented in Figure 3.18.
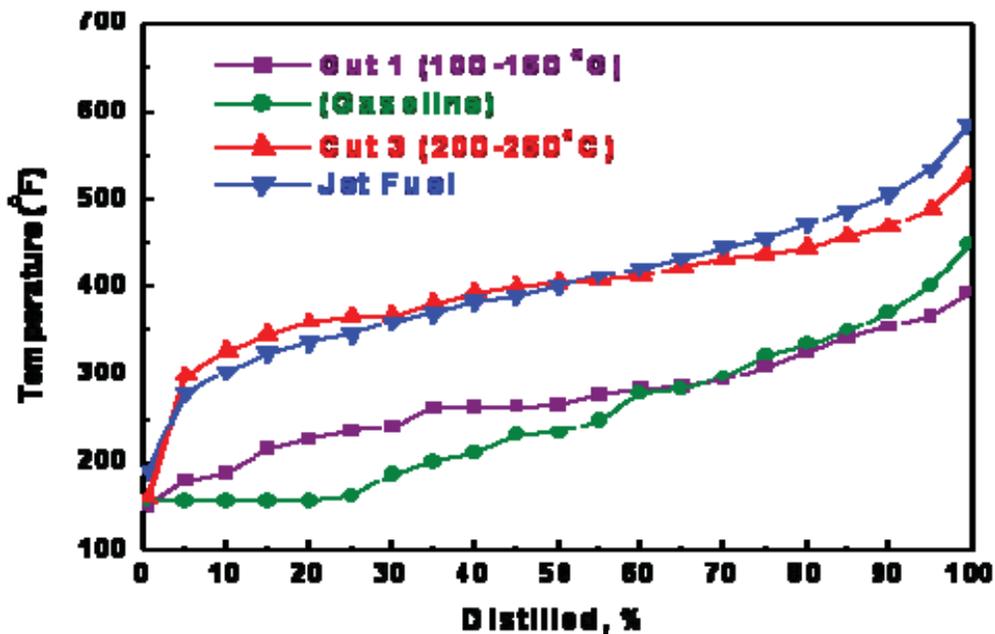
Figure 3.15   Comparison of fractional distillated fractions (100-150 and 200-250 ^{o}C) with gasoline and jet fuel by simulated distillation.
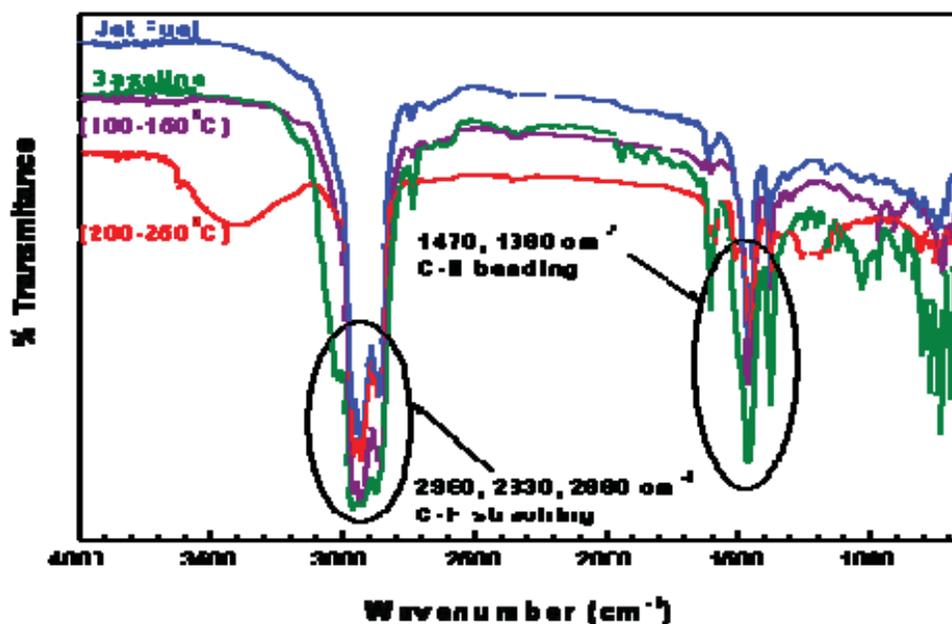
Figure 3.16   Comparison of FTIR spectral traces of 100-150 °C fraction, 200-250 °C
fraction, petroleum diesel and jet fuel.

Figure 3.16, compares FTIR spectral traces representing functional group compositional analysis from 100-150 °C, 200-250 °C with petroleum diesel and jet fuel. 3000-2800 and 1500-1400 cm^{-1} sharp peaks confirms the presence of alkanes in both 100-150 and 200-250 °C fractions. 3100-3000 and 1500-140 cm^{-1} sharp peaks confirm the presence of aromatic compounds present in both 100-150 and 200-250 °C fractions. These peaks are similar to petroleum diesel and gasoline. From the FTIR analysis, fractional distillated fractions 80-150 and 200-250 °C are very much correlated to the gasoline and jet fuel.

MSU-2 catalyst produces a hydrocarbon mix with zero oxygen content, very low or negligible acid value and energy value equivalent to that of petroleum fuels has a great potential for blending with petroleum hydrocarbons to provide drop-in fuels from biomass feedstocks via the pyrolysis and hydroprocessing route.

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3.8   Summary

Two catalysts, Como/Al and NiMo/Al, which are traditionally applied in both bio-oil hydrocracking in the petroleum refining industry for hydrocracking crude oil, were selected to compare to the performance of a proprietary catalyst developed at MSU, MSU-2. HC experiments were performed in a batch stirred autoclave at a temperature of 400 ^{o}C under 1000 psig hydrogen pressure with stirring at 1000 rpm. Catalyst weight for each experiment was 10 wt%. The objective of the experiments performed was to evaluate the most active catalyst that produces the optimum yield and quality of HC hydrocarbon mix.

Among the three catalysts tested, MSU-2 catalyst demonstrated better catalytic activity in terms of HC hydrocarbon mix yield (68 wt%) and percentage oxygen content with a zero value. CoMo/Al and NiMo/Al had significantly lower yields at about 66% for both. With regard to oxygen content Co/Mo/Al and NiMo/Al had significantly higher respective values of 3.0 and 1.8 wt%. MSU-2 also produced significantly lower char with a value of 3.5wt% compared to 6.5 and 7.2 wt% for NiMo/Al and CoMo/Al, respectively. Researchers have previously established that catalysts with acidic supports such as CoMo/Al and NiMo/Al produce substantial char during catalysis.

The major gas component produced by CoMo/Al and NiMo/Al was un-reacted hydrogen with respective percentages of 81.6 and 73.2 wt%. Surprisingly, the major gas component produced in the MSU-2 HC reaction was methane gas rather than unreacted hydrogen. The respective percentage of methane produced by MSU-2 was 50.2 wt% with the unreacted hydrogen gas component comprising 31.4 wt%. Only minor amounts of methane were produced by CoMo/Al and NiMo/Al with respective production of 2.3 and 2.5 wt% respectively. Previous research supports a conclusion that the possible pathway

for the methane formation was due to a methanation reaction initiated by the MSU-2 catalyst in the presence of hydrogen with the char carbon.

Further, HC process was optimized for MSU-2 catalyst with respect to reaction time. Experimental results indicates that a reaction time of 2 h was sufficient to achieve the desired zero oxygen content in the HC hydrocarbon mix. Longer reaction times led to a decrease in yields by converting the liquid product to gaseous components.

The energy efficiency of the HC of first-stage HT organic liquid from catalysis with MSU-2 was 93.61%. Actual hydrogen consumption was 232 NL/kg dry bio-oil. This value is 30% higher than the theoretical value calculated; this may be explained by the formation of high amounts of methane gas in the reaction with the expense of hydrogen.

The upgraded hydrocarbon mix contains zero water content, no oxygenated compounds and virtually zero oxygen. Total acid number is <0.1 and pH is nearly neutral at 6.5 with a viscosity and density equivalent to that of both petroleum diesel and gasoline. Higher heating value is almost similar than that of petroleum diesel. DHA analysis shows hydrocarbon mix contains paraffins and *iso*-paraffins (37%), napthenes (36%), aromatics (17%) and polynucleararomatics (PNAs) (11%). Zero olefins and no oxygenated compounds were identified among the 300 compounds characterized by the DHA. Simulated distillation of hydrocarbon mix results in distribution of these by fuel weights with gasoline comprising 37%, jet fuel 27%, diesel 25% and heavy fuel oil 11%. FTIR comparisons of petroleum gasoline and diesel to hydrocarbon mix indicate that it is composed of proportions of these fuels. ^{1}H-NMR spectra also showed the presence of aliphatic and aromatic hydrocarbon similar to those present in diesel fuel.

In later studies, the resultant hydrocarbon mix from HC process is distilled using spinning band distillation unit at respective boiling ranges. From this study, seven

fractions were collected between 50-100, 100-150,150-200, 200-250, 250-300, and 300-350 $^{\circ}$C and greater than 350 $^{\circ}$C. All these fractions were analyzed by GC/MS and FTIR and compared with gasoline, jet fuel and diesel fuel. From the analysis, the fraction obtained at 200-250 $^{\circ}$C has similar resemblance with jet fuel and the fraction obtained at 100-150 $^{\circ}$C has close relationship with gasoline fuel. The fraction obtained at temperature higher than 350 $^{\circ}$C is having properties similar to lubricated oil or bunker fuel.

The resultant hydrocarbon mix described here should be able to be refined in current petroleum refineries with minimal infrastructure modifications. In addition, it appears very feasible that sharp cuts of this hydrocarbon mix will allow production of fuels identical to petroleum diesel and gasoline such that blending of this product of biomass can be easily blended with petroleum fuels.

3.9   References

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CHAPTER IV

SUMMARY OF RESEARCH

The objective of this study was to upgrade the bio-oil to transportation fuels directly or for co-processing in standard refineries. Due to the presence of high amount of oxygenated compounds, bio-oil posses undesirable properties such as high acidity, high water content, low energy content, high viscosity, immiscibility with fossil fuels and polymerization during prolonged storage period. The negative properties are resolved by employing hydrodeoxygenation (HDO) in a two-stage process. First-stage mild hydrotreating (HT) will stabilize the bio-oil by removing water and highly reactive compounds and in second-stage hydrocracking (HC) hydrocarbons were formed by hydrocracking mechanism.

Chapter I gives an overview of hydroprocessing of bio-oil and its products. Chapter II describes an experimental study on HT of bio-oil. Catalyst screening experiments were performed using six commercially available heterogeneous catalysts and one proprietary catalyst. The reactions were performed out at 350 ^{o}C, 1500 psig, with 5 wt% catalyst for 4 h. Among all the hydrotreating catalysts tested, proprietary MSU-1 catalyst shows better catalytic activity in terms of highest organic liquid yield (38 wt%), organic liquid contains highest H/C ratio (1.65) and the second best low oxygen content (16.5 wt%). This was also further evident by the ANOVA statistical data analysis. Further, as a typical hydrotreating catalyst (NiMo/Al and CoMo/Al) MSU-1 does not need any presulfidation or sulfur in the feed prior to usage, and also it is 90% more cost

effective than the heterogeneous precious noble metal catalysts, thereby reducing the capital cost needed for hydrotreating catalyst in the mild hydrotreating process of bio-oil.

Later, HT process optimization studies with MSU-1 catalyst were performed with respect to temperature and reaction time. From the optimization studies it was found that a temperature of 350 $^{\circ}$C is sufficient to produce a light oil with the oxygen content of 17wt%, and also the reaction time of 1h is sufficient to produce high organic liquid yield of 41.2wt% with the oxygen content of 19 wt%. The calculated energy efficiency of the hydrotreating of bio-oil with MSU-1 catalyst is approximately 80%. From catalyst regeneration studies it was found that MSU-1 catalyst is highly stable and active with respect to multiple regenerations and is also effective in deoxygenation of the bio-oil to produce a quality organic liquid. . Hydrogen consumption of HT process is about 433 NL/kg dry bio-oil. This value is approximately 27% less than the previously reported literature value.

When compared with raw bio-oil the hydrotreated organic liquid contains 45% less acid value, 60% less oxygen, 78% less water content and higher heating value of twice that of the raw bio-oil. GC-MS analysis show reduced acids, phenols, aldehydes and ketones when compared with raw bio-oil and new hydrocarbon compounds are also formed. FTIR spectral data clearly distinguish the difference between raw bio-oil and hydrotreated organic liquid and similarities with diesel fuel were also observed. It is also shown from the ^{1}H-NMR spectra of hydrotreated organic liquid that formation of aliphatic hydrocarbons is evident.

In a subsequent study Chapter III, two catalysts, CoMo/Al and NiMo/Al, which are traditionally applied in both bio-oil hydrocracking in the petroleum refining industry for hydrocracking crude oil were selected to compare to the performance of a proprietary

catalyst developed at MSU, MSU-2. HC experiments were performed in a batch stirred autoclave at a temperature of 400 $^{\circ}$C under 1000 psig hydrogen pressure with stirring at 1000 rpm. Catalyst weight for each experiment was 10 wt%. The objective of the experiments performed was to evaluate the most active catalyst that produces the optimum yield and quality of HC hydrocarbon mix.

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The major gas component produced by CoMo/Al and NiMo/Al was un-reacted hydrogen with respective percentages of 81.6 and 73.2 wt%. Surprisingly, the major gas component produced in the MSU-2 HC reaction was methane gas rather than unreacted hydrogen. The respective percentage of methane produced by MSU-2 was 50.2 wt% with the unreacted hydrogen gas component comprising 31.4 wt%. Only minor amounts of methane were produced by CoMo/Al and NiMo/Al with respective production of 2.3 and 2.5 wt% respectively. Previous research supports a conclusion that the possible pathway for the methane formation was due to a methanation reaction initiated by the MSU-2 catalyst in the presence of hydrogen with the char carbon.

Further, HC process was optimized for MSU-2 catalyst with respect to reaction time. Experimental results indicates that a reaction time of 2 h was sufficient to achieve

the desired zero oxygen content in the HC hydrocarbon mix. Longer reaction times led to a decrease in yields by converting the liquid product to gaseous components.

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In later studies, the resultant hydrocarbon mix from HC process is distilled using spinning band distillation unit at respective boiling ranges. From this study, seven fractions were collected between 50-100, 100-150,150-200, 200-250, 250-300, and 300-350 ^{o}C and greater than 350 ^{o}C. All these fractions were analyzed by GC/MS and FTIR and compared with gasoline, jet fuel and diesel fuel. From the analysis, the fraction obtained at 200-250 ^{o}C has similar resemblance with jet fuel and the fraction obtained at

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100-150 ^{o}C has close relationship with gasoline fuel. The fraction obtained at temperature higher than 350 ^{o}C is having properties similar to lubricated oil or bunker fuel.

The resultant hydrocarbon mix described here should be able to be refined in current petroleum refineries with minimal infrastructure modifications. In addition, it appears very feasible that sharp cuts of this hydrocarbon mix will allow production of fuels identical to petroleum diesel and gasoline such that blending of this product of biomass can be easily blended with petroleum fuels.

APPENDIX A

HYDROTREATING OF RAW BIO-OIL

Table A.1   Mass balance results of HT of bio-oil by various heterogeneous catalysts,

Catalysts	Light oil	Heavy oil	Water	Char	Gas	Loss
Pd/C	36.55	0	45.71	7.66	9.08	1
Ru/C	32.03	0	37.29	10.79	18.89	1
MSU-1	37.93	0	40.37	7.32	13.38	1
CoMo/Al	0	36.6	44.17	5.91	11.32	2
NiMo/Al	34.7	0	42.84	4.37	16.09	2
Pt/Al	0	35.46	46.82	1.42	14.3	2
Pt/C	33.09	0	41.51	11.39	14.01	1

Table A.2   Physical and chemical properties of HT organic liquid with MSU-1 catalyst at various reaction times.

Property	1 h	2 h	3 h	4 h
acid value, mg KOH/g	61.49	58.0917	61.2993	59.44
water, wt%	3.964	3.45	3.46	2.26
HHV, MJ/kg	31.9826	33.4278	33.7963	34.4434
pH	3.56	3.8	3.83	3.93
Density, g/Ml	0.972	0.9652	0.9768	0.9623
C %	70.77	70.93	71.69	73.17
H%	9.44	10.29	10.89	10.09
N%	0.24	0.22	0.54	0.11
O%[a]	19.55	18.56	17.88	16.63

[a]by difference

A.1 Calculation of theoretical H_2 consumption and conversion from mass

(HT MSU-1, at 350°C, 1500 psig, 1 h is taken as an example)
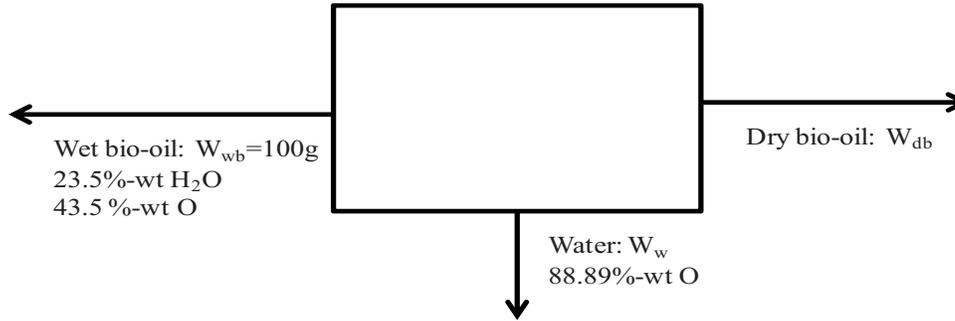
Overall mass balances:

$$W_{db} = W_{wb} - W_w = 100 - 0.235 \times 100 = 76.5 \text{ g}$$

Oxygen balances:

$$X_{O,db} = \frac{100 x 0.43 - 0.23 x 100 x 0.889}{76.5} x 100\% = 29.4\%$$

a) Weight oxygen actually removed from by HT reaction =29.4% x 77 g= 22.67 g

   (oxygen in water not participating in the reaction)

b) 22.67 g Oxygen = 1.41 mole Oxygen

c) Based on Eq. 1.1, amount of hydrogen needed to convert 1.41 moles of Oxygen= 1.41

   moles of hydrogen

d) Theoretical hydrogen consumption per kg dry bio-oil=

   mole Oxygen in dry bio-oil x 22.4 NL/Weight of dry bio-oil

   (1.41 mole x 22.4 NL/mole)/ (76.5x10^{-3}) = 412 NL/kg dry bio-oil.

A.2 Calculation of actual H_2 consumption

The actual hydrogen consumption (in moles) was calculated using the following

equation,

$$n_{i,t} = \frac{P_t V_{gas\text{-}space} \cdot X_{i,t}}{R.T_t}$$

$n_{i,t}$: mole of gas i at time t

P_t: total pressure of the reactor at time t

$V_{gas\text{-}space}$: volume of gas space within the reactor (=400 ml)

$X_{i,t}$: fraction of gas i at time t

T_t: temperature of reactor at time t

R: ideal gas constant: 8.314 J/(mol.K)

Initial conditions: Po= 103.42 bar, To= 25°C, $X_{H2,o}$= 100%.

    a) After the completion of the experiment: P_t= 53 bar at T_t=35 °C

    b) % H_2 in gas phase: $X_{H2,t}$= 70.5%-vol

        $N_{o,H2}$= ($P_{o,H2}$. $V_{gas\text{-}space}$) / (R. To) = 1.98

        $N_{t,H2}$= ($P_{t,H2}$. $V_{gas\text{-}space}$. $X_{H2,t)}$ / (R. To) = 0.5

        Overall hydrogen consumption: ΔN= $N_{o, H2}$ – $N_{t, H2}$ = 1.48

    c) <u>Actual hydrogen consumption per kg dry bio-oil</u> =

            mole oxygen in dry bio-oil x 22.4 NL/weight of dry bio-oil

        (1.48 mole x 22.4 NL/mole)/ (76.5×10^{-3}) = 433 NL/kg dry bio-oil.

APPENDIX B

HYDROCRACKING OF HYDROTREATED RAW BIO-OIL

B.1 **Calculation of theoretical H$_2$consumption and conversion from mass balance**

(HC MSU-2 at 400°C, 1000 psi, 2 h is taken as an example)

Weight of stabilized wet bio-oil: W$_{swb}$ = 100g
5 %-wt water
16.5 %-wt Oxygen

Weight of stabilized dry bio-oil: W$_{sdb}$

Water : W$_w$ =
88.89 %-wt
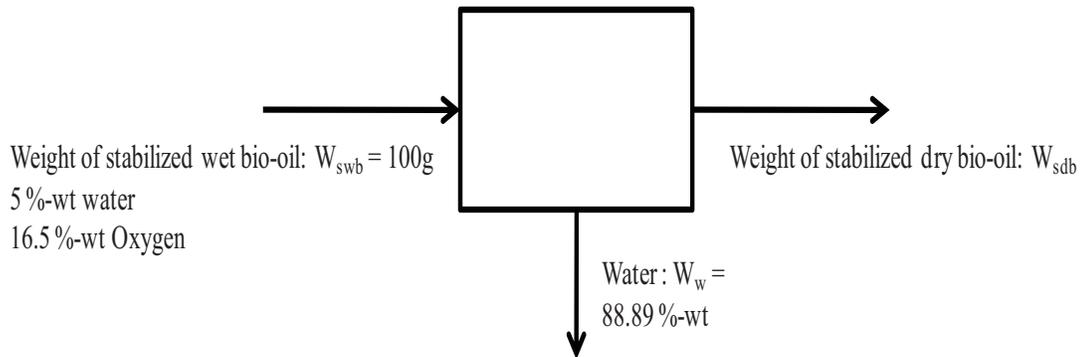
Overall mass balances:

$$W_{db} = W_{swb} - W_w = 100 - 0.05 \text{ x } 100 = 95 \text{ g}$$

Oxygen balances:

$$X_{O,db} = \frac{100x0.165 - 0.05x100x0.889}{95} x100\% = 0.12\%$$

a) Weight oxygen actually removed from by HC reaction 0.12% x 95 g= 12.05 g
   (oxygen in water not participating in the reaction)

b) 12.05 gram Oxygen = 0.75 mole Oxygen

c) Based on Eq. 1.1, amount of hydrogen needed to convert 0.75 moles of Oxygen= 0.75
   moles of hydrogen

d) Theoretical hydrogen consumption per kg dry bio-oil=

   mole Oxygen in dry bio-oil x 22.4NL/Weight of dry bio-oil

   (0.75   ole x 22.4 Nl/mole)/ (95x10^{-3}) = 177 NL/kg dry bio-oil.

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B.2 Calculation of actual H_2 consumption

The actual hydrogen consumption (in moles) was calculated using the following equation,

$$n_{i,t} = \frac{P_t V_{gas\text{-}space} \cdot X_{i,t}}{R.T_t}$$

$n_{i,t}$: mole of gas i at time t

P_t: total pressure of the reactor at time t

$V_{gas\text{-}space}$: volume of gas space within the reactor (=400 ml)

$X_{i,t}$: fraction of gas i at time t

T_t: temperature of reactor at time t

R: ideal gas constant: 8.314 J/(mol.K)

Initial conditions: Po= 71 bar, To= 25 $^{\circ}$C, $X_{H2,o}$= 100%.

a) After the completion of the experiment: P_t= 26 bar at T_t= 35 $^{\circ}$C

b) % H2 in gas phase: $X_{H2,t}$= 31.4%-vol

$N_{o,H2}$= ($P_{o,H2}$. $V_{gas\text{-}space}$) / (R. To) = 1.36

$N_{t,H2}$= ($P_{t,H2}$. $V_{gas\text{-}space}$. $X_{H2,t)}$ / (R. To) = 11.22

Overall hydrogen consumption: ΔN= $N_{o,H2}$ − $N_{t,H2}$ = 9.86

c) <u>Actual hydrogen consumption per kg dry bio-oil</u> =

mole Oxygen in dry bio-oil x 22.4 NL/weight of dry bio-oil

(9.86 mole x 22.4 Nl/mole)/ (76.5x10^{-3}) = 232 NL/kg dry bio-oil.

Table B.1   Complete report of DHA analyses of HC hydrocarbon mix with MSU-2 catalyst.

Peak No	Rt, mins	Area	Area %	Name
1	4.496	2095669	0.141	propane
2	4.590	1054953	0.071	isobutane
3	4.666	13880708	0.932	butane
4	4.936	7805908	0.524	isopentane
5	5.074	28821121	1.934	pentane
6	5.341	56882	0.004	unknown
7	5.621	23174021	1.555	cyclopentane
8	5.656	5461316	0.367	isohexane (2-methylpentane)
9	5.829	5451439	0.366	3-methylpentane
10	6.049	29411224	1.974	hexane
11	6.523	39608112	2.658	methylcyclopentane
12	7.006	13289547	0.892	benzene
13	7.113	74644	0.005	unknown
14	7.230	56281422	3.777	cyclohexane
15	7.386	3553044	0.238	2-methylhexane
16	7.454	871428	0.058	2,3-dimethylpentane
17	7.560	519784	0.035	1,1-dimethylcyclopentane
18	7.625	6299615	0.423	3-methylhexane
19	7.846	5263163	0.353	trans-1,3-dimethylcyclopentane
20	7.930	4673309	0.314	cis-1,3-dimethylcyclopentane
21	8.012	3758259	0.252	trans-1,2-dimethylcyclopentane
22	8.366	16899160	1.134	heptane
23	9.187	92355804	6.20	methylcyclohexane
24	9.292	378900	0.025	1,1,3-trimethylpentane
25	9.652	18656436	1.252	ethylcyclopentane
26	9.744	390517	0.026	dimethylhexane
27	10.043	1226268	0.082	1,2,4-trimethylcyclopentane
28	10.388	734263	0.049	1,2,3-trimethylcyclopentane
29	10.723	32624855	2.189	toluene
30	11.046	448470	0.030	2,3-dimethylhexane
31	11.124	383330	0.026	1,1,2-trimethylcyclopentane
32	11.342	2259074	0.152	2-methylheptane
33	11.422	1675640	0.112	4-methylheptane
34	11.519	282790	0.019	trans-1,3-dimethyl cyclohexane
35	11.738	3717725	0.249	3-methylheptane
36	11.799	1248554	0.084	dimethylhexane
37	11.864	8303189	0.557	cis-1,3-dimethylcyclohexane
38	11.964	2521495	0.169	trans-1,4-dimethylcyclohexane
39	12.268	538355	0.036	dimethylhexane
40	12.432	4986309	0.335	trans-1-ethyl-3-methylcyclopentane

Table B.1 (continued)

41	12.548	3690883	0.248	trans-1-ethyl-3-methylcyclopentane
42	12.617	3591951	0.241	1-ethyl-2-methylcyclopentane
43	12.741	458722	0.031	1-ethyl-1-methylcyclopentane
44	12.898	3561788	0.239	trans-1,3-dimethylcyclohexane
45	13.175	12738684	0.855	octane
46	13.281	6916668	0.464	cis-1,3-dimethylcyclohexane
47	13.652	1274755	0.086	methyl ethyl cyclopentane
48	14.219	1662065	0.112	cis-1-ethyl-2-methylcyclopentane
49	14.318	103461	0.007	C8-Naphthene
50	14.559	3200459	0.215	cis-1,2-dimethylcyclohexane
51	14.850	76265008	5.118	ethylcyclohexane
52	15.016	239371	0.016	unknown
53	15.141	403130	0.027	1,1,3-trimethylcyclohexane
54	15.243	804038	0.054	3,5-dimethylheptane
55	15.408	457796	0.031	c-1-ethyl-4-methylcyclohexane
56	15.479	667878	0.045	c-1-ethyl-2-methylcyclohexane
57	15.561	601482	0.040	t-1ethyl-4-methylcyclohexane
58	15.818	20805291	1.396	Ethylbenzene
59	15.976	878199	0.059	trimethyl cylco hexanes
60	16.095	664384	0.045	trimethyl cylco hexanes
61	16.184	351074	0.024	trimethyl cylco hexanes
62	16.299	11106204	0.745	p-Xylene
63	16.360	4171923	0.280	m-Xylene
64	16.494	177071	0.012	C9-aliphatics
65	16.531	150324	0.010	C9-aliphatics
66	16.634	1949700	0.131	C9-aliphatics
67	16.746	326543	0.022	C9-aliphatics
68	16.818	1593578	0.107	C9-aliphatics
69	16.876	1547211	0.104	C9-aliphatics
70	17.062	587013	0.039	C9-aliphatics
71	17.171	755749	0.051	C9-aliphatics
72	17.239	2686964	0.180	C9-aliphatics
73	17.307	513478	0.034	C9-aliphatics
74	17.525	6062832	0.407	o-xylene
75	17.615	512605	0.034	C9-aliphatics
76	17.738	324977	0.022	C9-aliphatics
77	17.854	5183059	0.348	C9-aliphatics
78	17.925	8981041	0.603	1-methyl-c-4-ethylcyclohexane
79	18.047	2258525	0.152	C9-aliphatics
80	18.190	697515	0.047	C9-aliphatics
81	18.268	2464332	0.165	C9-aliphatics
82	18.600	171185	0.011	C9-aliphatics

Table B.1 (continued)

83	18.771	8420283	0.565	C9-aliphatics
84	18.936	5846427	0.392	C9-aliphatics
85	19.089	1670081	0.112	C9-aliphatics
86	19.315	1179329	0.079	C9-aliphatics
87	19.447	1120649	0.075	C9-aliphatics
88	19.492	1074882	0.072	C9-aliphatics
89	19.600	2326109	0.156	C9-aliphatics
90	19.732	1080108	0.072	C9-aliphatics
91	19.827	519677	0.035	C9-aliphatics
92	20.057	1462755	0.098	C9-aliphatics
93	20.179	67533427	4.532	propylcyclohexane
94	20.379	8712854	0.585	butylcyclopentane
95	20.461	408205	0.027	C9-aliphatics
96	20.575	260532	0.017	C9-aliphatics
97	20.646	1046634	0.070	C9-aliphatics
98	20.845	24558878	1.648	n-propylbenzene
99	20.929	473444	0.032	C9-aliphatics
100	20.988	675218	0.045	C9-aliphatics
101	21.052	467291	0.031	C9-aliphatics
102	21.124	540647	0.036	C9-aliphatics
103	21.238	8740436	0.587	1-methyl-3-ethylbenzene
104	21.334	4863860	0.326	1-methyl-2-ethylbenzene
105	21.635	1274988	0.086	mix C10's(arom-Naphthenes*iso-paraffins)
106	21.714	814765	0.055	mix C10's(arom-Naphthenes*iso-paraffins)
107	21.792	357625	0.024	mix C10's(arom-Naphthenes*iso-paraffins)
108	21.890	828262	0.056	mix C10's(arom-Naphthenes*iso-paraffins)
109	21.933	476819	0.032	mix C10's(arom-Naphthenes*iso-paraffins)
110	22.021	1097989	0.074	mix C10's(arom-Naphthenes*iso-paraffins)
111	22.092	2076664	0.139	mix C10's(arom-Naphthenes*iso-paraffins)
112	22.152	877301	0.059	mix C10's(arom-Naphthenes*iso-paraffins)
113	22.244	642706	0.043	mix C10's(arom-Naphthenes*iso-paraffins)
114	22.313	559458	0.04	mix C10's(arom-Naphthenes*iso-paraffins)
115	22.466	3382244	0.227	mix C10's(arom-Naphthenes*iso-paraffins)
116	22.547	1286862	0.086	mix C10's(arom-Naphthenes*iso-paraffins)
117	22.689	284617	0.019	mix C10's(arom-Naphthenes*iso-paraffins)
118	22.832	3044443	0.204	mix C10's(arom-Naphthenes*iso-paraffins)
119	22.905	9829052	0.660	mix C10's(arom-Naphthenes*iso-paraffins)
120	23.044	5441094	0.365	mix C10's(arom-Naphthenes*iso-paraffins)
121	23.093	1354868	0.091	mix C10's(arom-Naphthenes*iso-paraffins)
122	23.162	1283132	0.086	mix C10's(arom-Naphthenes*iso-paraffins)
123	23.284	3263972	0.219	mix C10's(arom-Naphthenes*iso-paraffins)
124	23.471	1523009	0.102	mix C10's(arom-Naphthenes*iso-paraffins)

Table B.1 (continued)

125	23.553	2535095	0.170	mix C10's(arom-Naphthenes*iso-paraffins)
126	23.711	4938699	0.331	mix C10's(arom-Naphthenes*iso-paraffins)
127	23.840	4345364	0.292	N-C10
128	23.924	1791523	0.120	mix C10's(arom-Naphthenes*iso-paraffins)
129	24.026	1784921	0.120	mix C10's(arom-Naphthenes*iso-paraffins)
130	24.116	1433625	0.096	mix C10's(arom-Naphthenes*iso-paraffins)
131	24.214	1674156	0.112	mix C10's(arom-Naphthenes*iso-paraffins)
132	24.348	1433421	0.096	mix C10's(arom-Naphthenes*iso-paraffins)
133	24.436	583958	0.0	mix C10's(arom-Naphthenes*iso-paraffins)
134	24.602	5690821	0.382	Indane
135	24.727	654114	0.044	mix C10's(arom-Naphthenes*iso-paraffins)
136	24.818	2034791	0.137	mix C10's(arom-Naphthenes*iso-paraffins)
137	24.909	216837	0.015	mix C10's(arom-Naphthenes*iso-paraffins)
138	24.971	678072	0.046	mix C10's(arom-Naphthenes*iso-paraffins)
139	25.165	9468131	0.635	n-butylcyclohexane
140	25.248	555527	0.037	mix C11's(arom-Naphthenes*iso-paraffins)
141	25.359	6384974	0.429	mix C11's(arom-Naphthenes*iso-paraffins)
142	25.445	3297359	0.221	mix C11's(arom-Naphthenes*iso-paraffins)
143	25.556	6677068	0.448	mix C11's(arom-Naphthenes*iso-paraffins)
144	25.639	1583778	0.106	mix C11's(arom-Naphthenes*iso-paraffins)
145	25.762	7703381	0.517	mix C11's(arom-Naphthenes*iso-paraffins)
146	25.864	933989	0.063	mix C11's(arom-Naphthenes*iso-paraffins)
147	25.947	370820	0.025	mix C11's(arom-Naphthenes*iso-paraffins)
148	26.062	4773236	0.320	mix C11's(arom-Naphthenes*iso-paraffins)
149	26.218	4075801	0.274	mix C11's(arom-Naphthenes*iso-paraffins)
150	26.386	494624	0.033	mix C11's(arom-Naphthenes*iso-paraffins)
151	26.482	626005	0.042	mix C11's(arom-Naphthenes*iso-paraffins)
152	26.544	824854	0.055	mix C11's(arom-Naphthenes*iso-paraffins)
153	26.610	1101719	0.074	mix C11's(arom-Naphthenes*iso-paraffins)
154	26.674	819991	0.055	mix C11's(arom-Naphthenes*iso-paraffins)
155	26.739	3272777	0.220	mix C11's(arom-Naphthenes*iso-paraffins)
156	26.872	471261	0.032	mix C11's(arom-Naphthenes*iso-paraffins)
157	26.951	3028231	0.203	mix C11's(arom-Naphthenes*iso-paraffins)
158	27.025	2264837	0.152	mix C11's(arom-Naphthenes*iso-paraffins)
159	27.183	1580206	0.106	mix C11's(arom-Naphthenes*iso-paraffins)
160	27.242	706981	0.05	mix C11's(arom-Naphthenes*iso-paraffins)
161	27.522	2729371	0.183	mix C11's(arom-Naphthenes*iso-paraffins)
162	27.584	704765	0.047	mix C11's(arom-Naphthenes*iso-paraffins)
163	27.699	2997694	0.201	mix C11's(arom-Naphthenes*iso-paraffins)
164	27.772	3184417	0.214	mix C11's(arom-Naphthenes*iso-paraffins)
165	27.865	2280639	0.153	mix C11's(arom-Naphthenes*iso-paraffins)
166	27.924	3190522	0.214	mix C11's(arom-Naphthenes*iso-paraffins)

Table B.1 (continued)

167	28.061	3082879	0.207	mix C11's(arom-Naphthenes*iso-paraffins)
168	28.179	2653529	0.178	mix C11's(arom-Naphthenes*iso-paraffins)
169	28.279	3275444	0.220	n-C11
170	28.392	1488418	0.100	mix C11's(arom-Naphthenes*iso-paraffins)
171	28.498	1039627	0.070	mix C11's(arom-Naphthenes*iso-paraffins)
172	28.583	3508397	0.235	mix C11's(arom-Naphthenes*iso-paraffins)
173	28.686	816334	0.055	mix C11's(arom-Naphthenes*iso-paraffins)
174	28.773	1527469	0.103	mix C11's(arom-Naphthenes*iso-paraffins)
175	28.932	971478	0.065	mix C11's(arom-Naphthenes*iso-paraffins)
176	29.086	1098297	0.074	mix C11's(arom-Naphthenes*iso-paraffins)
177	29.330	7022053	0.471	mix C11's(arom-Naphthenes*iso-paraffins)
178	29.422	252573	0.017	mix C11's(arom-Naphthenes*iso-paraffins)
179	29.760	13600087	0.913	penyl cyclo hexane
180	29.967	3238848	0.217	mix C11's(arom-Naphthenes*iso-paraffins)
181	30.084	3020475	0.203	mix C11's(arom-Naphthenes*iso-paraffins)
182	30.221	8854042	0.594	tetra hydro Naphthalene
183	30.312	5864986	0.394	tetra hydro Naphthalene
184	30.549	1063732	0.071	tetra hydro Naphthalene
185	30.610	822540	0.055	tetra hydro Naphthalene
186	30.684	876980	0.059	tetra hydro Naphthalene
187	30.797	1439984	0.097	tetra hydro Naphthalene
188	30.874	836333	0.056	tetra hydro Naphthalene
189	30.974	677369	0.045	tetra hydro Naphthalene
190	31.163	2179280	0.146	Naphthalene
191	31.292	481338	0.032	multi hydro PNA's
192	31.402	697134	0.047	multi hydro PNA's
193	31.539	1496303	0.100	multi hydro PNA's
194	31.765	3243057	0.218	multi hydro PNA's
195	31.843	1355390	0.091	multi hydro PNA's
196	32.036	1682901	0.113	multi hydro PNA's
197	32.102	985044	0.066	multi hydro PNA's
198	32.189	394716	0.026	multi hydro PNA's
199	32.288	1379240	0.093	multi hydro PNA's
200	32.417	1105235	0.074	multi hydro PNA's
201	32.510	3961583	0.266	multi hydro PNA's
202	32.651	496415	0.033	multi hydro PNA's
203	32.764	2738232	0.184	multi hydro PNA's
204	32.986	1177537	0.079	multi hydro PNA's
205	33.056	648193	0.044	multi hydro PNA's
206	33.144	4905828	0.329	multi hydro PNA's
207	33.258	2412914	0.162	multi hydro PNA's
208	33.512	4167033	0.280	multi hydro PNA's

Table B.1 (continued)

209	33.622	544614	0.037	multi hydro PNA's
210	33.737	1301552	0.087	multi hydro PNA's
211	33.820	594327	0.040	multi hydro PNA's
212	33.897	646471	0.043	multi hydro PNA's
213	33.956	1234194	0.083	multi hydro PNA's
214	34.068	634865	0.043	multi hydro PNA's
215	34.182	2201616	0.148	multi hydro PNA's
216	34.315	560665	0.038	multi hydro PNA's
217	34.459	1347127	0.090	multi hydro PNA's
218	34.540	1798098	0.121	multi hydro PNA's
219	34.652	6184373	0.415	multi hydro PNA's
220	34.755	3296628	0.221	multi hydro PNA's
221	34.912	1606832	0.108	multi hydro PNA's
222	34.975	8189594	0.550	multi hydro PNA's
223	35.051	917292	0.062	multi hydro PNA's
224	35.163	974445	0.065	multi hydro PNA's
225	35.227	968805	0.065	multi hydro PNA's
226	35.331	1258320	0.084	multi hydro PNA's
227	35.440	1603477	0.108	multi hydro PNA's
228	35.498	787406	0.053	multi hydro PNA's
229	35.586	547923	0.037	multi hydro PNA's
230	35.708	6475928	0.435	multi hydro PNA's
231	35.799	1018296	0.068	multi hydro PNA's
232	35.894	782808	0.053	multi hydro PNA's
233	35.961	2143338	0.144	multi hydro PNA's
234	36.029	868870	0.058	multi hydro PNA's
235	36.092	2103591	0.141	multi hydro PNA's
236	36.135	1582555	0.106	multi hydro PNA's
237	36.226	1400154	0.094	multi hydro PNA's
238	36.269	708906	0.048	multi hydro PNA's
239	36.318	1538241	0.103	multi hydro PNA's
240	36.416	4795337	0.322	multi hydro PNA's
241	36.488	5025333	0.337	multi hydro PNA's
242	36.558	908765	0.061	multi hydro PNA's
243	36.620	3483094	0.234	multi hydro PNA's
244	36.727	1034432	0.069	multi hydro PNA's
245	36.776	883718	0.059	multi hydro PNA's
246	36.849	579625	0.039	multi hydro PNA's
247	36.898	782301	0.053	multi hydro PNA's
248	36.966	1843447	0.124	multi hydro PNA's
249	37.025	2683192	0.180	multi hydro PNA's
250	37.108	928337	0.062	multi hydro PNA's

Table B.1 (continued)

251	37.206	1532734	0.103	multi hydro PNA's
252	37.315	6756178	0.453	multi hydro PNA's
253	37.451	990832	0.066	multi hydro PNA's
254	37.503	3103593	0.208	multi hydro PNA's
255	37.594	3168309	0.213	multi hydro PNA's
256	37.721	3074061	0.206	multi hydro PNA's
257	37.776	1767549	0.119	multi hydro PNA's
258	37.889	1300250	0.087	multi hydro PNA's
259	37.945	3490844	0.234	multi hydro PNA's
260	38.019	1883239	0.126	multi hydro PNA's
261	38.098	1329121	0.089	multi hydro PNA's
262	38.202	6742000	0.452	dicyclohxylmethane
263	38.273	2301519	0.154	N-C15
264	38.326	1770193	0.119	multi hydro PNA's & cyclics(C11-16)
265	38.384	4450676	0.299	multi hydro PNA's & cyclics(C11-16)
266	38.485	2367395	0.159	multi hydro PNA's & cyclics(C11-16)
267	38.524	3561687	0.239	multi hydro PNA's & cyclics(C11-16)
268	38.634	3531523	0.237	multi hydro PNA's & cyclics(C11-16)
269	38.714	2474633	0.166	multi hydro PNA's & cyclics(C11-16)
270	38.820	1626760	0.109	multi hydro PNA's & cyclics(C11-16)
271	38.866	1706508	0.115	multi hydro PNA's & cyclics(C11-16)
272	38.931	2586388	0.174	multi hydro PNA's & cyclics(C11-16)
273	38.984	2366494	0.159	multi hydro PNA's & cyclics(C11-16)
274	39.052	2013027	0.135	multi hydro PNA's & cyclics(C11-16)
275	39.117	4744433	0.318	multi hydro PNA's & cyclics(C11-16)
276	39.177	2157312	0.145	multi hydro PNA's & cyclics(C11-16)
277	39.236	2547848	0.171	multi hydro PNA's & cyclics(C11-16)
278	39.296	1892220	0.127	multi hydro PNA's & cyclics(C11-16)
279	39.359	3119714	0.209	multi hydro PNA's & cyclics(C11-16)
280	39.457	2443174	0.164	multi hydro PNA's & cyclics(C11-16)
281	39.498	1888430	0.127	multi hydro PNA's & cyclics(C11-16)
282	39.547	934343	0.063	multi hydro PNA's & cyclics(C11-16)
283	39.638	2673510	0.179	multi hydro PNA's & cyclics(C11-16)
284	39.680	3432668	0.230	multi hydro PNA's & cyclics(C11-16)
285	39.741	1534235	0.103	multi hydro PNA's & cyclics(C11-16)
286	39.820	25934237	1.740	n-C16
287	39.943	8321617	0.558	1-phenyl-2-cyclohexylethane
288	40.014	1237260	0.083	mix hydrocarobons(C17-C18)
289	40.053	1676503	0.113	mix hydrocarobons(C17-C18)
290	40.106	1592204	0.107	mix hydrocarobons(C17-C18)
291	40.142	1683466	0.113	mix hydrocarobons(C17-C18)
292	40.209	2291038	0.154	mix hydrocarobons(C17-C18)

Table B.1 (continued)

293	40.341	8370945	0.562	mix hydrocarobons(C17-C18)
294	40.464	8959162	0.601	mix hydrocarobons(C17-C18)
295	40.549	3672122	0.246	mix hydrocarobons(C17-C18)
296	40.606	2501792	0.168	mix hydrocarobons(C17-C18)
297	40.646	5475121	0.367	mix hydrocarobons(C17-C18)
298	40.738	3277400	0.220	mix hydrocarobons(C17-C18)
299	40.840	4368456	0.293	mix hydrocarobons(C17-C18)
300	40.885	2058007	0.138	mix hydrocarobons(C17-C18)
301	40.938	8232428	0.552	mix hydrocarobons(C17-C18)
302	41.024	2946711	0.198	mix hydrocarobons(C17-C18)
303	41.077	6689439	0.449	mix hydrocarobons(C17-C18)
304	41.172	5399546	0.362	mix hydrocarobons(C17-C18)
305	41.240	2914370	0.196	mix hydrocarobons(C17-C18)
306	41.306	2905794	0.195	mix hydrocarobons(C17-C18)
307	41.418	7063784	0.474	mix hydrocarobons(C17-C18)
308	41.560	8398383	0.564	mix hydrocarobons(C17-C18)
309	41.621	3906996	0.262	mix hydrocarobons(C17-C18)
310	41.688	3815793	0.256	mix hydrocarobons(C17-C18)
311	41.769	2557259	0.172	mix hydrocarobons(C17-C18)
312	41.875	39857060	2.675	n-C17
313	42.019	4752614	0.319	heavier hydrocarbons(C18-C20)
314	42.118	8483221	0.569	heavier hydrocarbons(C18-C20)
315	42.247	4771282	0.320	heavier hydrocarbons(C18-C20)
316	42.355	3353522	0.225	heavier hydrocarbons(C18-C20)
317	42.393	2648664	0.178	heavier hydrocarbons(C18-C20)
318	42.422	2324752	0.156	heavier hydrocarbons(C18-C20)
319	42.470	3889124	0.261	heavier hydrocarbons(C18-C20)
320	42.527	3706155	0.249	heavier hydrocarbons(C18-C20)
321	42.597	2172364	0.146	heavier hydrocarbons(C18-C20)
322	42.679	5877655	0.394	octadecane
323	42.739	4024789	0.270	heavier hydrocarbons(C18-C20)
324	42.814	1462395	0.098	heavier hydrocarbons(C18-C20)
325	42.888	4372151	0.293	heavier hydrocarbons(C18-C20)
326	42.957	3176373	0.213	heavier hydrocarbons(C18-C20)
327	43.001	3751268	0.252	heavier hydrocarbons(C18-C20)
328	43.062	3323992	0.223	heavier hydrocarbons(C18-C20)
329	43.221	5504712	0.369	heavier hydrocarbons(C18-C20)
330	43.269	2519667	0.169	heavier hydrocarbons(C18-C20)
331	43.309	3487649	0.234	heavier hydrocarbons(C18-C20)
332	43.411	4534022	0.304	heavier hydrocarbons(C18-C20)
333	43.473	1579589	0.106	heavier hydrocarbons(C18-C20)
334	43.521	2407669	0.162	heavier hydrocarbons(C18-C20)

Table B.1 (continued)

335	43.612	2709856	0.182	heavier hydrocarbons(C18-C20)
336	43.666	1569255	0.105	heavier hydrocarbons(C18-C20)
337	43.753	3204816	0.215	heavier hydrocarbons(C18-C20)
338	43.800	1732845	0.116	heavier hydrocarbons(C18-C20)
339	43.854	1435744	0.096	heavier hydrocarbons(C18-C20)
340	43.963	3200158	0.215	heavier hydrocarbons(C18-C20)
341	44.060	2556398	0.172	heavier hydrocarbons(C18-C20)
342	44.121	2010905	0.135	heavier hydrocarbons(C18-C20)
343	44.207	1600070	0.107	heavier hydrocarbons(C18-C20)
344	44.261	1319755	0.089	heavier hydrocarbons(C18-C20)
345	44.423	1070340	0.072	heavier hydrocarbons(C18-C20)
346	44.504	1616608	0.108	heavier hydrocarbons(C18-C20)
347	44.580	1082340	0.073	heavier hydrocarbons(C18-C20)
348	44.649	1392987	0.093	heavier hydrocarbons(C18-C20)
349	44.720	951628	0.064	heavier hydrocarbons(C18-C20)
350	44.782	738393	0.050	heavier hydrocarbons(C18-C20)
351	44.836	1577416	0.106	heavier hydrocarbons(C18-C20)
352	44.983	1377780	0.092	heavier hydrocarbons(C18-C20)
353	45.150	1112040	0.075	heavier hydrocarbons(C18-C20)
354	45.317	524902	0.035	heavier hydrocarbons(C18-C20)
355	45.392	546230	0.037	heavier hydrocarbons(C18-C20)
356	45.585	852950	0.057	heavier hydrocarbons(C18-C20)
357	45.762	418976	0.028	heavier hydrocarbons(C18-C20)
358	45.892	237968	0.016	heavier hydrocarbons(C18-C20)
359	45.965	327059	0.022	heavier hydrocarbons(C18-C20)
360	46.148	174554	0.012	heavier hydrocarbons(C18-C20)
361	46.405	509189	0.034	heavier hydrocarbons(C18-C20)
362	47.329	127035	0.009	heavier hydrocarbons(C18-C20)
363	48.395	116237	0.008	heavier hydrocarbons(C18-C20)
Totals		1490072064	99.995	