2010

# Hydrodeoxygenation process for converting glycerol into bio-crude / by Matthew A. Tymchyshyn.

Tymchyshyn, Matthew Alexander

---

http://knowledgecommons.lakeheadu.ca/handle/2453/3939

# Hydrodeoxygenation Process for Converting Glycerol into Bio-crude

**By**
**Matthew A. Tymchyshyn**

**Supervisor:**
**Dr. C. Charles Xu**

**Environmental Engineering**
**Lakehead University**
**Thunder Bay, Ontario, Canada.**
**August 10, 2010**

Library and Archives
Canada

Published Heritage
Branch

395 Wellington Street
Ottawa ON K1A 0N4
Canada

Bibliothèque et
Archives Canada

Direction du
Patrimoine de l'édition

395, rue Wellington
Ottawa ON K1A 0N4
Canada

*Your file Votre référence*
*ISBN:* 978-0-494-71915-2
*Our file Notre référence*
*ISBN:* 978-0-494-71915-2

NOTICE:

The author has granted a non-exclusive license allowing Library and Archives Canada to reproduce, publish, archive, preserve, conserve, communicate to the public by telecommunication or on the Internet, loan, distribute and sell theses worldwide, for commercial or non-commercial purposes, in microform, paper, electronic and/or any other formats.

The author retains copyright ownership and moral rights in this thesis. Neither the thesis nor substantial extracts from it may be printed or otherwise reproduced without the author's permission.

AVIS:

L'auteur a accordé une licence non exclusive permettant à la Bibliothèque et Archives Canada de reproduire, publier, archiver, sauvegarder, conserver, transmettre au public par télécommunication ou par l'Internet, prêter, distribuer et vendre des thèses partout dans le monde, à des fins commerciales ou autres, sur support microforme, papier, électronique et/ou autres formats.

L'auteur conserve la propriété du droit d'auteur et des droits moraux qui protège cette thèse. Ni la thèse ni des extraits substantiels de celle-ci ne doivent être imprimés ou autrement reproduits sans son autorisation.

In compliance with the Canadian Privacy Act some supporting forms may have been removed from this thesis.

While these forms may be included in the document page count, their removal does not represent any loss of content from the thesis.

Conformément à la loi canadienne sur la protection de la vie privée, quelques formulaires secondaires ont été enlevés de cette thèse.

Bien que ces formulaires aient inclus dans la pagination, il n'y aura aucun contenu manquant.

Canada

# Abstract

Bio-energy is a clean (containing negligible sulfur and being near-carbon neutral), renewable and abundant source of energy. Bio-energy can be a potential alternative to fossil fuels for the production of energy and chemicals. Due to the world's increasing energy demands, declining petroleum reserves and growing concerns over the detrimental environmental effects of fossil fuels, there is an increased interest in the production of bio-fuels (bio-ethanol, bio-diesel and bio-oils) from biomass feedstocks. The increased production of bio-diesel by trans-esterification of vegetable oils has resulted in a glut of glycerol as a by-product. Economically beneficial utilization of the glycerol would greatly enhance bio-diesel plant production economics.

Part I of this research investigated the effectiveness of various catalysts in the conversion of glycerol into bio-crude at elevated temperature and pressure. The reactions were carried out in an autoclave micro-reactor at a temperature of 300°C and an initial pressure of hydrogen of 5 MPa. Gaseous products were collected and analyzed by Micro-GC. The solid products were removed by filtration while the liquid products were separated into water soluble products (unreacted glycerol, acids, alcohols) and water insoluble products (bio-oil/bio-crude) by extraction with water and ethyl acetate. The bio-crude obtained was comprehensively characterized to determine its physical/chemical properties.

The support materials: MgO, AC (activated carbon), $\gamma$-$Al_2O_3$ and X-type zeolite were found to have a negligible catalytic effect by themselves, with a maximum bio-oil yield of 3.7 wt.% for the zeolite when tested without catalyst metals. Subsequent experiments with catalyst metals revealed a positive correlation between support acidity and bio-oil yield. This effect was confirmed by upgrading glycerol in the presence of acidified zeolite which produced a remarkably higher yield of bio-oil (~34 wt.%) even without metal catalyst loading. Co, Ru and Mo were found to be the almost equally effective metal catalysts, increasing bio-oil yield to ~13 wt.% when loaded on to $Al_2O_3$. Ru was found to greatly increase glycerol gasification. The most effective combination of metals and support for the hydrodeoxygenation (HDO) of glycerol was determined to be MoCoP/zeolite achieving a maximum bio-oil yield of ~40 wt.%. The role of phosphorus as a catalyst promoter was discussed. Sulfidation and reduction of the MoCoP/zeolite catalyst resulted in drastic reductions in bio-oil yield contrary to results reported in published literature. The bio-oil products were found to consist mostly of substituted phenols, ketones, and to a lesser extent alcohols, ethers and cycloalkanes. The bio-oil had a higher carbon contents and much lower oxygen contents than the glycerol feedstock. The bio-oils reached a maximum HHV of 33 MJ/kg.

In Part II of this research, the HDO of glycerol into bio-crude was investigated in order to determine the optimum conditions required to produce high quality (low oxygen) bio-oil. These experiments were conducted using the best catalyst out of those tested in Part I (MoCoP/Zeolite) and investigated the effects of residence time, reaction temperature, hydrogen pressure, and solvent on bio-oil yield. The reaction products of these experiments were characterized in a similar manner to Part I. The fresh catalysts were characterized by ICP-AES, $N_2$ isothermal adsorption, XRD and spent catalysts were characterized by XRD and TGA. The optimum conditions for the hydrodeoxygenation of glycerol into bio-crude in the presence of MoCoP/zeolite catalyst were found to be: 300°C reaction temperature, 5 MPa initial hydrogen pressure, 60 min reaction time and 100% glycerol feed. While dilution of the glycerol feedstock with water had a negative effect on bio-oil yield, HDO of pure glycerol produced the highest bio-oil yield (40 wt.% at 300°C, 1 h and 5 MPa $H_2$). The amount of char deposited on the spent catalyst decreased with extended reaction time, increased reaction temperature, and elevated initial hydrogen pressure.

*Keywords*: Glycerol; Bio-crude; Hydrodeoxygenation; Hydro-treating, Catalysts

# Acknowledgements

I would like to express my sincere appreciation and the deepest gratitude to my supervisor, Professor C. Charles Xu, for his encouragement, expert guidance, and invaluable advice during the course of my Masters studies.

I am grateful for the financial support from Dr. Xu through the research assistantships made possible by the Discovery Grant awarded to Prof. Xu from the Natural Science and Engineering Research Council of Canada (NSERC) and the New Directions Research Program fund from the Ontario Ministry of Agricultural, Foods and Rural Affairs (OMAFRA).

I sincerely acknowledge all professors in the Department of Chemical Engineering and the Graduate Program in Environmental Engineering, especially, Professors B. Liao, B.H. Kjartanson and L. Catalan, for their instruction in my course of study and their helpful comments on my research. I'm also deeply grateful to Dr. Catalan for the loan of his sand bath which enabled the timely completion of this research when the LUGEL sand bath malfunctioned. I am also very grateful to the examiners, Dr. Lionel Catalan and Dr. Mathew Leitch, for their time and effort in critiquing this thesis.

I wish to thank Dr. Z. Yuan for his helpful discussions, suggestions, instruction, and assistance over the course of my research. I would also like to express my gratitude to Mr. Amandeep Parmar, Ms. Linghong Zhang, Ms. Shuna Cheng and the other students in Prof. Xu's Green Energy Laboratory at Lakehead University for their generous assistance in the course of my studies and research towards this work. Very special thanks are extended to Mr. Kailash Bhatia of the Department of Mechanical Engineering and Mr. Garry Rathje of the Department of Chemical Engineering for their great assistance in constructing and maintaining the experimental equipment used in my experiments.

Last but not least, I'd like to thank Mr. Allan MacKenzie, Mr. Ain Raitsakas and Mr. Keith Pringnitz at the Lakehead University Instrumentation Lab for their assistance with the XRD, CHN, CNS and ICP-AES analyses.

# Table of Contents

# List of Tables

# List of Figures

# CHAPTER 1

# Introduction

## 1.1 Background

### *1.1.1 Bio-energy and Biomass Conversion Technologies*

Over the past century a majority of the world's energy demands was met by fossil fuels, comprising: 30% petroleum, 23% natural gas, 22% coal, 6% nuclear, and 19% renewable (Song, 2002). Chemical industries and energy production based on fossil fuel resources is expected to gradually phase out over the course of the 21st century due to the depletion of the fossil resources that these industries rely on (Okkerse and Van Bekkum, 1999). Due to the continuing decline in fossil fuel resources and increasing concerns over greenhouse gas emissions and energy security, there has been a resurgence of interest in renewable bio-energy. Biomass feedstocks such as agricultural/forestry residues and woodwastes (harvest residues, slash, sawdust, bark, etc.) have the potential to be a large source for energy, fuels, chemicals and materials (Karagoz et al., 2005; Ogi and Yokohama, 1993). Many countries have legislation set in place to promote the use of biomass energy and bio-fuels. For example, the Canadian federal government has enacted a target of 5% ethanol in gasoline by 2010, which will require the production of more than 300 million litres of cellulosic ethanol per year to meet this target. The European Union has set an objective to substitute conventional fuels with biomass-derived fuels (bio-fuels) in the transport sector with a market share of 5.75% by the end of 2010 (EU Directive 2003/30/EC). In December 2007, then President Bush of the U.S.A. signed into law a Renewable Fuels Standard (RFS) that calls for at least 36 billion gallons of ethanol and other bio-fuels to be used nationwide by 2022, including a minimum of 9 billion gallons in 2008, and 20.5 billion gallons by 2015 or about 15% replacement of the U.S.A.'s gasoline consumption.

Bio-energy is a blanket term that refers to all forms of renewable energy that are derived from biomass feedstocks. Biomass feedstocks typically have a heating value comparable to that of low rank coal (lignite and sub-bituminous coals). The heating values range from 8 MJ/kg for green matter to between 17-23 MJ/kg for dry plant matter. The earth's natural biomass of 150 billion metric tons of dry biomass replacement represents an energy supply of around 3000 EJ ($3\times10^{21}$ J) per year, or about 6 times the world's total energy consumption. Although these resources are renewable, carbon-neutral, and remarkably abundant, they are also very bulky and difficult to transport, handle, and store. In order to make use of these resources it is, therefore, necessary to develop cost-effective technologies to convert them into liquid bio-fuels of a higher energy density and other valuable chemicals (Yamazaki et al., 2006).

Biomass conversion technologies may be classified into two major categories: bio-chemical processes and thermo-chemical processes (Figure 1-1) (Sharma and Bakshi, 1991; Bridgwater, 1991; Holt and Van der Burgt, 1998). Biologically-based technologies use acid/engineered enzymes to break down ligno-cellulosic materials with the aim of hydrolyzing the cellulose into glucose that can be fermented into ethanol. The development of new enzymes is still at the research stage, and most of the enzymes and the microorganisms that have been developed are strongly dependent on the chemical composition of the feedstocks, and are therefore applicable only to specific homogenous feedstocks. As a result, current fermentation-based technology does not make the cellulosic ethanol production economically viable. In addition, the blending of high ratios of fuel alcohol into gasoline would require the modification of existing engines and delivery systems (Holt and Van der Burgt, 1998).

Thermo-chemical processes for the production of liquid bio-fuels include indirect liquefaction processes e.g. gasification combined with various catalytic processes for production of synthetic fuels (e.g., methanol, ethanol and high quality diesel), and direct liquefaction technologies mainly pyrolysis and high pressure liquefaction processes.

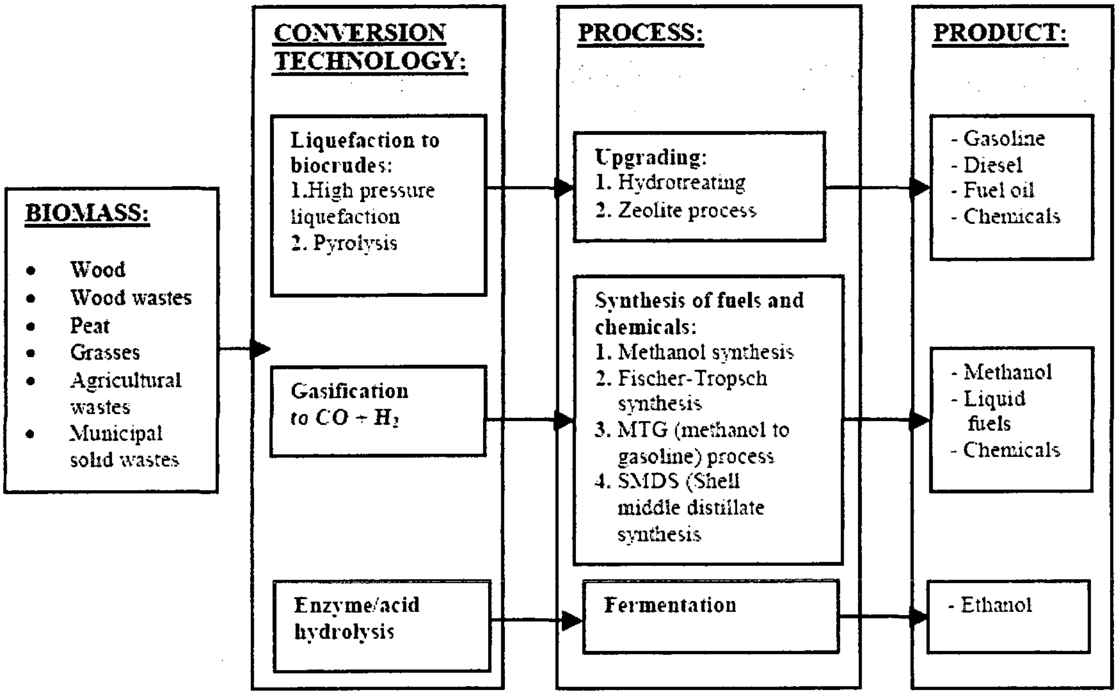


Figure 1-1. Routes from biomass to fuels and chemicals (Sharma and Bakshi, 1991; Bridgwater, 1991; Holt and Van der Burgt, 1998)

Direct liquefaction of biomass followed by upgrading and refining is regarded as a promising approach in addition to the indirect liquefaction processes such as the MTG process (Mobil methanol to gasoline process) and the SMDS process (Shell middle distillate synthesis process), currently under development. Direct liquefaction of biomass for the production of bio-oil/bio-crude has attracted increasing interest in recent years due to increasing crude oil price and increasing concerns over greenhouse gas emissions. The bio-oil/bio-crude products from direct liquefaction can be upgraded into high quality liquid transportation fuels (Sharma and Bakshi, 1991).

Fast pyrolysis (operating at low pressures of 0.1-0.5 MPa but high temperatures >500°C) is currently the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils have high oxygen and water contents and only about half the caloric content of petroleum (<20 MJ/kg,).

High-pressure liquefaction technology, on the other hand, normally operates at moderate temperatures <400°C but high pressures of 5-20 MPa in the presence of suitable solvents (water or organics) and a catalyst and has the potential for producing liquid oils (also called bio-oils or bio-crudes) with much higher caloric values (25-35 MJ/kg) (Yamazaki et al., 2006; Xu and Etcheverry, 2008).

Bio-oils/bio-crudes are a complex mixture of oxygen-containing compounds in the form of phenol and benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols which all contribute to the oxygen content of the oil (Appel et al., 1969; Minowa et al., 1998; Qu et al., 2003). In addition, water originating from both the moisture originally present in the feedstock as well as water produced during the pyrolysis and direct liquefaction processes adds to the oxygen content in bio-oil or bio-crude (Bridgwater, 2003; Czernik and Bridgwater, 2004). The total oxygen content of bio-oils can be as high as 40-50 wt% for pyrolysis oils compared to 20-30 wt% for bio-crudes from high-pressure liquefaction processes, depending on the origin of the biomass and the process conditions, e.g. temperature, residence time, heating rate and the catalysts used (Bridgwater, 1994; Furimsky, 2000). The presence of high levels of oxygen in bio-oils is a limitation in their use as liquid transportation fuels since high oxygen contents result in high viscosity, low heating value, poor thermal and chemical stability, corrosivity (due to organic acids present) and immiscibility with hydrocarbon fuels (Bridgwater, 2003; Czernik and Bridgwater, 2004; Yaman, 2004). The bio-crudes/bio-oils must therefore be upgraded by reducing or completely eliminating their oxygen content (Bridgwater, 1994; Bridgwater, 1996).

Two typical technologies for upgrading of bio-oils for fuel applications include catalytic cracking and catalytic hydro-treating. Catalytic cracking processes, using cracking catalysts (zeolites, silica–alumina and molecular sieves), are performed at or near atmospheric pressure without the addition of hydrogen. The advantages of low-pressure operation without the need of hydrogen, i.e. lower equipment costs and lack of expensive hydrogen, have attracted much interest in the literature on the upgrading of bio-oils (Adjave and Bakhshi, 1995a and 1995b; Katikaneni et al., 1995; Williams and Horne, 1995; Adjave et al., 1996). However, the yield of hydrocarbon oils is very low because of high yields of both char/coke and tars. In addition, the deposition of these undesirable products on the catalyst results in gradual catalyst deactivation and necessitates periodical or continual regeneration of the catalysts. In contrast, catalytic hydro-treating processes operate at high pressures under a hydrogen atmosphere and/or in the presence of hydrogen donor solvents (Baker and Elliott, 1996; Craig and Coxworth, 1987; Maggi and Delmon, 1993). Over the past 20 years, significant efforts have been made in hydrodeoxygenation (HDO) of biomass-derived oils. Research into the catalytic chemistry and kinetics of the hydrotreating of various model compounds containing oxygen, such as phenolic compounds and aromatic ethers, have been reviewed by Furimsky (2000) and Elliott (2007).

### *1.1.2 Bio-diesel and By-product Utilization*

Bio-diesel is an alternative to petroleum fuels and other bio-fuels that is rapidly increasing in popularity. Many countries have legislation set in place to promote the use of bio-diesel as a substitute for the petroleum-derived diesel fuel. For example, the production of 500 million litres of biodiesel is planned in Canada (Valliyappan et al., 2008), and the provinces of Manitoba and British Columbia have already mandated blending of percentages of biodiesel in their provincial diesel supplies, 2% and 5% respectively. The province of Alberta plans to follow this trend with its own mandate of 2% of biodiesel being blended in its diesel supply by the summer of 2010 (CRFA, 2009).

Hydro-treatment of both fresh and spent vegetable oils for the production of bio-diesel has been investigated. For example, Murata et al. (2010) produced a synthetic diesel fuel by hydrotreating jatropha oil. They obtained ~80% carbon molar yield of diesel range compounds but required a 1:1 ratio of catalyst to oil. Decreasing the catalyst-to-oil ratio to a more practical 1:10 ratio decreased the yield to 2.3%. High oil-to-catalyst ratios were also found to occasionally produce hydrogenated triglycerides rather than straight-chain alkanes. It is also possible to hydro-treat vegetable oils directly, which eliminates the production of glycerol.

Most bio-diesel is produced by trans-esterification of seed oils with methanol. The process produces methyl esters of long chain hydrocarbons and glycerol as a byproduct (as displayed in Figure 1-2). Glycerol (1,2,3-propanetriol) is a clear, viscous liquid that freezes at 17°C and boils at 290°C. Approximately 1 kg of glycerol is produced for every 9 kg of bio-diesel formed (Dasari et al., 2005).

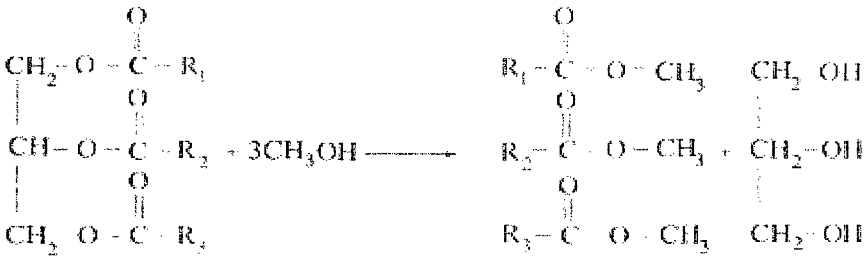


Figure 1-2. Transesterification of tri-glycerides into bio-diesel

Increased production of bio-diesel has led to a drastic increase in the availability of glycerol, 100,000 tonnes annually in the U.S.A. alone. As a result the cost of glycerol decreased from \$2.50/lb. in 2004 to ~30¢/lb. in 2006 (Yazdani and Gonzalez, 2007). In 2005 the global glycerol market was 800,000 tons with 400,000 tons coming from biodiesel in comparison to only 60,000 tons from biodiesel in 2001 (Pagliaro et al., 2007).

Glycerol has of course been used in various applications before the recent increase in its availability (Figure 1-3). These applications include: polyol-based flexible foams, anti-freeze and aircraft de-icers, unsaturated polyester resins, explosives in the form of smokeless gunpowder, cordite and dynamite, medical and medicinal uses including heart medication (as glycerol trinitrate), the vitrification of samples for cold storage and the conditioning of dialysis membranes as well as food uses such as a diabetic sweetener, humectant and emulsifier.

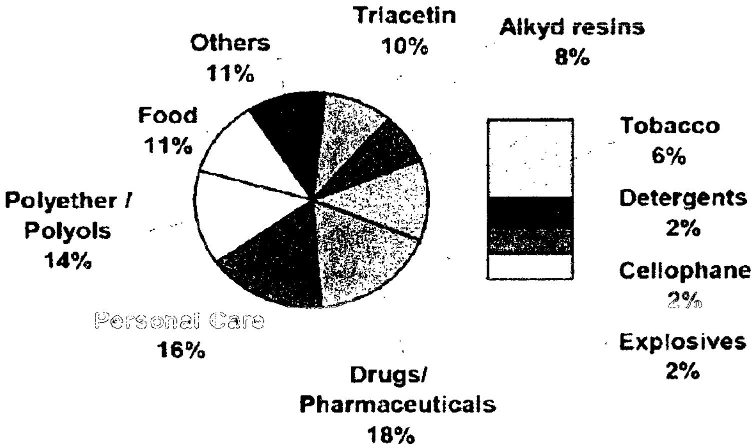


Figure 1-3. Industrial uses of glycerol (Novaol, 2002)

As a result of its growing availability and decreased cost, there is increasing interest in the use of glycerol as an economical feedstock for various chemicals and bio-fuels. Much of the research involving glycerol has focussed on converting glycerol into hydrogen, syngas for subsequent Fisher-Tropsch synthesis, or other value-added products such as propylene glycol, acrolein, oxygenates (esters and ethers) for use as fuel additives, and various alcohols (Figure 1-

4). Glycerol as an oxygenated organic compound can be a promising feedstock for the production of liquid transportation fuels by oligomerization and de-oxygenation. However, there is no research available in the published literature on this topic.

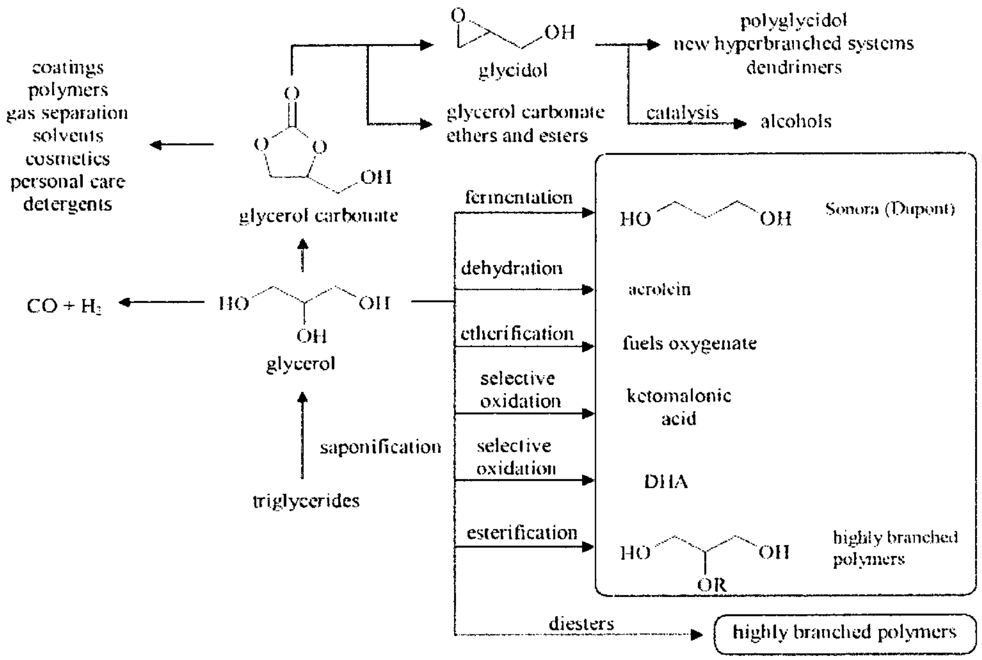


Figure 1-4. Products derived from Glycerol (Pagliaro et al., 2007)

In contrast to the current practice of glycerol gasification into syngas and subsequent synthesis into hydrocarbon fuels, or conversion of glycerol into various chemicals, the primary objective of this work was to investigate the direct conversion of glycerol into high energy, low oxygen bio-crude under moderate conditions via oligomerization and de-oxygenation.

## 1.2 Research Objectives

As discussed in the previous section, the main objectives of the present work ae summarized below:

(1) To produce high quality bio-crude by concurrent dehydration, oligomerization and hydrodeoxygenation of glycerol, and;

(2) To determine the optimum reaction conditions (type of catalysts, reaction temperature, reaction time, hydrogen pressure, and solvent effects) of the glycerol conversion process.

## 1.3 Organization of the Thesis

This thesis is composed of five chapters.

**Chapter 1 - Introduction**. This section provides a general introduction and a brief review of the literature relevant to the present research describing the research background, the latest advances in glycerol research, and the objectives of the present work.

**Chapter 2 - Literature Review**. This is a detailed literature review on the fields of research related to the present study. Specifically these include: direct liquefaction of biomass into bio-crude, upgrading of bio-crude/model compounds by catalytic hydrodeoxygenation (HDO), and current research into the utilization of glycerol.

**Chapter 3 - Hydrodeoxygenation of Glycerol into Bio-crude: Catalyst Screening.**

**Chapter 4 - Hydrodeoxygenation of Glycerol into Bio-crude: Process Optimization.**

**Chapter 5 - Conclusions**. This section presents the overall conclusions of this research and recommendations for future work.

## References

Adjave JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts. *Fuel Process. Technol.* **45** (1995)a 161-183.

Adjave JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part II: Comparative catalyst performance and reaction pathways. *Fuel Process. Technol.* **45** (1995)b 185-202.

Adjave JD, Katikaneni SPR, Bakhshi NN. Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution. *Fuel Process. Technol.* **48** (1996) 115-143.

Appel HR, Wender I, Miller RD. Conversion of urban refuse to oil. *US Bureau of Mines, Technical Progress Report* (1969) No. 25.

Baker EG, Elliott DC. Research in thermochemical biomass conversion. London: Elsevier Applied Science (1988) 883.

Bridgwater AV, Double JM. Production costs of liquid fuels from biomass. *Fuel* **70** (1991) 1209-1224.

Bridgwater AV. Catalysis in thermal biomass conversion. *Appl. Catal. A: Gen.* **116** (1994) 5-47.

Bridgwater AV. Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. *Catal. Today* **29** (1996) 285-295.

Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* **91** (2003) 87-102.

Craig W, Coxworth E. Proceedings of the sixth canadian bioenergy R&D seminar. London: Elsevier Applied Science (1987) 407.

CRFA, Manitoba Fuels Change with New Biodiesel Mandate (2009).

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

Dasari, MA. et al., Low-pressure hydrogenolysis of glycerol to propylene glycol, *Applied Catalysis A: General* **281** (2005) 225–231.

Elliott DC. Historical developments in hydroprocessing bio-oils. *Energy Fuels* **21** (2007) 1792-1815.

EU Directive 2003/30/EC, The promotion of the use of biofuels and other renewable fuels for transport., 8 May 2003.

Furimsky E. Review: catalytic hydrodeoxygenation. *Appl. Catal. A: Gen.* **199** (2000) 147-190.

Holt NA, Van Der Burgt MJ. Proceedings of power production from biomass III, gasification and pyrolysis R&D&D for industry (VTT Symposium 192). Espoo, Finland, 14-15 September, 1998; 163-177.

Karagoz S, Bhaskar T, Muto A, Sakata Y, Oshiki T, Kishimoto T. Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. *Chem. Eng. J.* **108** (2005) 127-137.

Katikaneni SPR, Adjave JD, Bakhshi NN. Performance of aluminophosphate molecular sieve catalysts for the production of hydrocarbons from wood-derived and vegetable oils. *Energy Fuels* **9** (1995) 1065-1078.

Maggi R, Delmon B. Advances in thermochemical biomass conversion. London: Elsevier Applied Science (1993) 1185.

Minowa T, Kondo T, Sudirjo ST. Thermochemical liquefaction of Indonesia biomass residues. *Biomass Bioenergy* **14** (1998) 517-524.

Murata K., Liu Y., Inaba M., Takahara I. Production of Synthetic Diesel by Hydrotreatment of Jatropha Oils Using Pt-Re/H-ZSM-5 Catalyst Energy *Fuels* **24** (2010) 2404–2409.

Novaol, May 2002.

Ogi T, Yokoyama S. Liguid fuel production from woody biomass by direct liquefaction. *Sekiyu Gakkaishi* **36** (1993) 73.

Okkerse C, Van Bekkum H. Fossil to green. *Green Chem.* **1** (1999) 107-114.

Pagliaro M. et al. From Glycerol to Value-Added Products *Angew. Chem. Int. Ed.* **46** (2007) 4434 – 4440

Qu Y, Wei X, Zhong C. Experimental study on the direct liquefaction of Cunninghamia Lanceolata in water. *Energy* **28** (2003) 597-606.

Sharma RK, Bakhshi NN. Catalytic upgrading of biomass-derived oils to transportation fuels and chemical. *Can. J. Chem. Eng.* **69** (1991) 1071-1108.

Song C. Fuel processing for low-temperature and high-temperature fuel cells: challenges and opportunities for sustainable development in the 21st century. *Catal. Today* **77** (2002) 17-49.

Valliyappan T, Bakhshi NN, Dalai AK Pyrolysis of glycerol for the production of hydrogen or syn gas, *Bioresource Technology* **99** (2008) 4476–4483.

Williams PT, Horne PA. The influence of catalyst regeneration on the composition of zeolite-upgraded biomass pyrolysis oils. *Fuel* **74** (1995) 1839-1851.

Xu C., Etcheverry T. Hydro-liquefaction of woody biomass in sub- and super-critical ethanol with iron-based catalysts. *Fuel* **87** (2008) 335-345.

Yamazaki J, Minami E, Saka S. Liquefaction of beech wood in various supercritical alcohols. *J Wood Sci* **52** (2006) 527-532.

Yazdani, SS, Gonzalez, R. Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry *Current Opinion in Biotechnology* **18** (2007) 213–219.

# CHAPTER 2

# Literature Review on the Production and Upgrading of Bio-oils/Bio-crude from Biomass via Direct Liquefaction and Glycerol Utilization

## 2.1 Introduction

Direct liquefaction of biomass for the production of bio-oil/bio-crude has attracted increasing interest in recent years due to rising crude oil prices and increasing concerns over greenhouse gas emissions. Pyrolysis and high pressure liquefaction are the two main thermo-chemical technologies that have been developed for the direct liquefaction of biomass into bio-oil or bio-crude products. Fast pyrolysis (operated at a moderate pressures of 0.1-0.5 MPa and temperatures >500°C) is, so far, the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils contain high levels of oxygenated compounds and water and therefore have only about half of the caloric value (<20 MJ/kg) of petroleum. High-pressure liquefaction technology with a suitable solvent (water or organic) plus catalyst, operating at moderate temperatures (<400°C) but higher pressures of 5-20 MPa, has the potential to produce liquid oils (also called bio-oils or bio-crudes) with much higher caloric values (25-35 MJ/kg).

Pyrolysis oils and bio-oils/bio-crudes are composed of a complex mixture of oxygen-containing compounds in the form of phenol and benzene derivatives, hydroxyketones, carboxylic acids and esters, aldehydes as well as aliphatic and aromatic alcohols. These compounds contribute to the high oxygen content of bio-oil (up to 30-50 wt.%), and result in not only a lower calorific value, but increased viscosity, poor thermal and chemical stability, corrosivity (due to organic acids) and immiscibility with hydrocarbon fuels. To produce high-quality bio-oils for use as liquid transportation fuels, pyrolysis oils/bio-crudes must be upgraded by various means to reduce their oxygen content.

Bio-diesel is a more environmentally friendly and near carbon-neutral alternative to petroleum diesel. Its use is increasing as the public and governments become more environmentally aware. The rapid increase in bio-diesel production has led to an associated increase in the availability of the glycerol - a byproduct of the trans-esterification process used to produce bio-diesel. The increased availability of glycerol has prompted much research into using the glycerol as a novel and cost effective feedstock for the production of various chemicals.

The objective of this review is to provide an overview of the thermo-chemical direct liquefaction technologies used in the production of bio-oils/bio-crudes from biomass, the development of the upgrading technologies to produce high quality liquid transport fuels from bio-oils/bio-crudes, as well as the current research into glycerol utilization and the potential conversion of glycerol into bio-crude oils.

## 2.2 Bio-oil Production via Fast Pyrolysis

Thermochemical conversion of biomass into liquid fuels and valuable chemicals can be achieved by either pyrolysis or high-pressure liquefaction (Molten et al., 2003; Demirbas, 2000). Pyrolysis of biomass is performed in an inert atmosphere at high temperatures, typically 400-800°C, and at low pressures around 0.1-0.5 MPa without the addition of any catalyst. At these high temperatures, solid lignocellulosic materials thermally decompose into smaller fragments which combine to produce oily compounds, yielding about 50-75 wt.% liquid products (pyrolysis oil or bio-oil). As a side note, the yield of bio-oil (or other liquid or solid products) is usually presented as wt.%, i.e. mass of product as a fraction of the mass of feedstock. In the case of gaseous products, the yield is usually expressed as mol%. Heat is usually added indirectly, although partial gasification and combustion of the feedstock may be employed to give direct heating. Gas and char are produced in addition to the liquid products. The relative proportions of gas, liquid and solid products depend on the pyrolysis parameters specifically heating rate and final temperature. Fast or flash pyrolysis (with a high heating rate and short vapor residence time) is used to maximize liquid products (Bridgwater, 1991). Flash pyrolysis produces liquid yields up to 75 wt.% at relatively low temperatures, typically 500°C but less than 650°C, and at very high heating rates of 1,000 °C/s, or even 10,000 °C/s, and very short residence times of typically less than 1 s. The rapid heating and rapid quenching in fast pyrolysis processes produce intermediate liquid products, which condense to form liquid oil products before being further broken down into gaseous products. The high heating rates also minimize char formation, and no char is formed under some conditions (Demirbas, 2005). Increasing flash pyrolysis temperature above 700°C leads to still higher heating and reaction rates but results in very high gas product yields of up to 80 wt.% (Bridgwater, 1992).

Over the past twenty years, research into fast or flash pyrolysis has shown that high yields of liquid and gas products, including valuable chemicals or chemical intermediates and fuels, can be obtained from various biomass feedstocks including agricultural/forest residues and waste streams (Bridgwater et al.,. 2001). Fast pyrolysis bio-oils are complex mixtures of compounds derived from the depolymerization and degradation of cellulose, hemi-cellulose and lignin (Zhang et al., 2007; Oasmaa and Czernik, 1999; Czernik and Bridgwater, 2004). The typical properties of pyrolysis bio-oils and of a petroleum-based heavy fuel oil are shown in Table 2-1. Bio-oil from fast pyrolysis is a complex mixture composed of acids, alcohols, aldehydes, esters, furans, guaiacols, ketones, sugars, syringols, lignin-derived phenols and extractible terpenes

(Guo et al., 2001). Zhang et al. (2001) separated the bio-oil into four fractions: aliphatic, aromatic, and polar compounds as well as non-volatiles by using solvent extraction and liquid chromatography on an aluminum column. Analysis of the fractions indicated the presence of high levels of acetic acid and hydroxyacetones in the aqueous phase, with less polar components and aromatic hydrocarbons in the oil phase. In general, fast pyrolysis bio-oils are a complex mixture of highly oxygenated compounds with a broad distribution of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids and alcohols (Peng and Wu, 2000).

Table 2-1. Typical properties of pyrolysis bio-oil (before upgrading) and of a petroleum-based heavy fuel oil (Czernik and Bridgwater, 2004)

| Physical property | Bio-oil | Heavy fuel oil |
|---|---|---|
| Moisture content (wt.%) | 15-30 | 0.1 |
| pH | 2.5 | - |
| Specific gravity | 1.2 | 0.94 |
| Elemental composition (wt.%) | | |
| C | 54-58 | 85 |
| H | 5.5-7.0 | 11 |
| O | 35-40 | 1.0 |
| N | 0-0.2 | 0.3 |
| Ash | 0-0.2 | 0.1 |
| HHV (MJ/kg) | 16-19 | 40 |
| Viscosity (at 50 °C, cP) | 40-100 | 180 |

Fast pyrolysis is, so far, the only industrially realized technology for the production of bio-oils from biomass. A fast pyrolysis process employing circulating fluidized beds, originally developed at the University of Western Ontario is now commercialized by Ensyn Technologies in Renfrew, Ontario (RTP, rapid thermal processing). Also in Canada, another fast pyrolysis technology based on a fluidized bed has been commercialized by Dynamotive Energy Systems Corp., which has a demonstration project at Erie Flooring and Wood Products in Ontario. However, pyrolysis oils contain high levels of oxygen/water and therefore have lower caloric values only about half of that of petroleum (<20 MJ/kg). In addition the presence of organic acids makes them strongly acidic and corrosive. As a result, pyrolysis oils are not regarded as an ideal liquid fuel for heat or power generation, and without upgrading, cannot be used as a liquid transportation fuels.

The water content of bio-oil can be as high as 15–30 wt.% and comes from moisture initially present in the feedstock and also as the product of dehydration reactions during pyrolysis and later storage. The presence of water decreases the heating value of the oil as well as the combustion flame temperature of the fuel (Scholze and Meier, 2001). The removal of water from pyrolysis oil by evaporation is problematic, because heating bio-oil results in the rapid polymerization of components in the bio-oil and the associated increased viscosity.

It is the presence of high levels of oxygen in bio-oils that is the principal difference between bio-oils and hydrocarbon fuels. The high oxygen content of bio-oil results in its lower energy density compared to conventional fossil fuels and is responsible for its immiscibility with hydrocarbon fuels. In addition, the presence of substantial amounts of carboxylic acids, such as formic and acetic acid, contributes to bio-oil pH values as low as 2–3 (Sipilae et al., 1998). This makes bio-oils corrosive and the problem is exacerbated at elevated temperatures. This imposes more stringent requirements in the choice of construction materials of bio-oil storage vessels and necessitates significant upgrading before it can be used as a transportation fuel (Zhang et al., 2007).

## 2.3 High-pressure Liquefaction Technology for Bio-crude Production

In contrast to fast pyrolysis, high-pressure liquefaction is performed under an inert or, preferably, a reducing atmosphere at moderate temperatures less than 400°C, but higher pressures ranging between 5 and 20 MPa. In high-pressure liquefaction processes, the macro-molecular compounds in the feedstock are decomposed into small fragments in the presence of suitable solvent(s) i.e. water, alcohols, alkanes, phenols, or tetralin, etc. and a suitable catalyst. The molecular fragments produced in the reaction are unstable and reactive, and tend to re-polymerize into oily compounds having various molecular weights (Molten, 1983). The presence of a suitable solvent is critical for a direct liquefaction process, as the solvent can act a diluting agent for the products formed and/or fragment stabilization agent to prevent from re-polymerization/condensation reactions to form char or a heavy residuum.

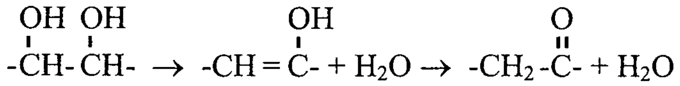
High-pressure liquefaction is a superior direct liquefaction technology compared with fast pyrolysis, in that it produces higher quality bio-oil with more desirable chemical and physical properties. High-pressure liquefaction technology also has the potential for producing heavy liquid oils or bio-crudes with increased heating values and a range of other value-added chemicals including vanillin, phenols, aldehydes, and acetic acid etc. Appell et al. (1971) at the Pittsburgh Energy Technology Center (PETC) reported effective high-pressure liquefaction of a variety of lignocellulosic materials into oily products in water at an elevated temperature in the presence of CO and $Na_2CO_3$ catalyst. The PETC's research into direct liquefaction of biomass was further advanced by the research group at the Pacific Northwest National Laboratory (PNNL) in the U.S.A. led by Dr. D. C. Elliott. During the 1980's, much work on scaling up the pioneer work by Appell et al. and on utilizing the direct liquefaction oil products (Elliott, 1980; Schirmer et al., 1984) was done at PNNL.

High-pressure direct liquefaction processes are normally operated at moderate temperatures (200-450°C), pressures greater than 1 MPa and using longer residence times (10-60 min) in hot compressed water (Qu et al., 2003; Karagoz et al., 2004; Boocock et al., 1979; Yokohama et al., 1984; Minowa et al., 1998) or organic solvents such as anthracene oil (Appel et al., 1969; Crofcheck et al., 2005), alcohols (methanol, ethanol, propanol and butanol) and acetone, etc (EU Directive 2003/30/EC; Cemek and Kucuk, 2001; Miller et al., 1999). Typical yields of liquid products for high-pressure liquefaction processes are in the range of 20-60 wt.%. Although high-pressure liquefaction processes produce lower yields of heavy oil (bio-crude) compared with fast pyrolysis processes (which yield 40-75 wt.% bio-oil with a HHV of about 20 MJ/kg), the bio-crude products have much higher caloric values (HHV= ~30 MJ/kg) (Qu et al., 2003; Minowa et al., 1998). Higher heating value (HHV) is also known as the gross calorific value or gross energy of a fuel. It is defined as the amount of heat released by a specified quantity of fuel (initially at 25°C) once it is combusted and the products have returned to a temperature of 25°C. This takes into account the latent heat of vapourization of any water that is produced during combustion. When comparing the gross energy yield (oil yield × HHV), the two types of direct liquefaction processes are comparable. The yields of bio-crude depend on many operating parameters including reaction temperature, pressure, residence time, type of solvents and the catalysts employed. Alkaline solutions, e.g., $Na_2CO_3$, NaOH, $K_2CO_3$, KOH, LiOH, RbOH, CsOH, and $Ca(OH)_2$, etc., have been widely employed as catalysts in direct liquefaction processes to suppress the formation of char while enhancing the yield of liquid products (Karagoz et al., 2004). Very little research, however, has been reported on the roles that catalysts play in direct liquefaction processes. Appell et al. (1967) proposed the following mechanism for sodium carbonate-catalyzed liquefaction of carbohydrates in the presence of carbon monoxide.

*Sodium carbonate and water react with carbon monoxide, to yield sodium formate:*

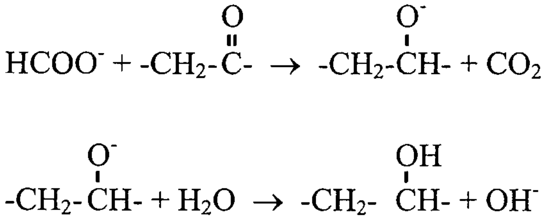
$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCOO^-Na^+ + CO_2$

*Dehydration of adjacent hydroxyl groups in the carbohydrate to form an enol, followed by isomerization to ketone:*



$$-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}- \rightarrow -\mathrm{CH}=\overset{\mathrm{OH}}{\overset{|}{\mathrm{C}}}- + H_2O \rightarrow -CH_2-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}- + H_2O$$

*Reduction of the newly formed carbonyl group to the corresponding alcohol with formate ion and water*



$$HCOO^- + -CH_2-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}- \rightarrow -CH_2-\overset{\mathrm{O^-}}{\overset{|}{\mathrm{CH}}}- + CO_2$$

$$-CH_2-\overset{\mathrm{O^-}}{\overset{|}{\mathrm{CH}}}- + H_2O \rightarrow -CH_2-\overset{\mathrm{OH}}{\overset{|}{\mathrm{CH}}}- + OH^-$$

*Hydroxyl ions react with an additional carbon monoxide molecule to regenerate the formate ion*

$OH^- + CO \rightarrow HCOO^-$

According to this mechanism, deoxygenation of carbohydrates occurs via decarboxylation of an ester formed by hydroxyl groups and formate ions derived from carbonate. In addition, alkali salts, such as sodium carbonate and potassium carbonate, can also catalyze hydrolysis of macromolecules, such as cellulose and hemicellulose, into smaller fragments (Chornet, 1985). The micelle-like fragments produced by hydrolysis are then degraded to smaller compounds by dehydration, dehydrogenation, and decarboxylation.

Glycerine has been used as a solvent for the direct liquefaction of beech wood with the presence of $Na_2CO_3$ or KOH as the catalyst (Demirbas, 2000). The most important variables appeared to be temperature, the amount of alkali and the nominal reaction time. In the presence of $Na_2CO_3$, a very high total oil yield of 68.4 wt.% was obtained, but the solubility of the as-produced high polarity oil in gasoline was found to be very low (less than 2 wt.%).

Hot-compressed water (as the most environmentally friendly and safest reagent) has been widely researched as the solvent for biomass direct liquefaction. The addition of an alkaline salt such as NaOH, $Na_2CO_3$, KOH and $K_2CO_3$ has been found to significantly promote oil yields. Qu et al. (2003) carried out direct liquefaction of Chinese fir in water in an autoclave at 280–360°C and for 10–30 min, with a maximum heavy oil yield of 24 wt.% obtained at 320°C after 10 min reaction time. The effect of reaction temperature on the yield of heavy oil was found to be less significant in the range of 280–360°C. However, the addition of catalyst and/or hydrogen, to stabilize the intermediate liquid products, were very effective in increasing the yield of heavy oil. Karagoz et al. (2005) performed hydrothermal treatment of woody biomass at 280°C for 15 min in the presence of alkaline solutions (NaOH, $Na_2CO_3$, KOH and $K_2CO_3$). Based on biomass conversion levels and the yield of liquid products, the following sequence of catalytic activity was observed: $K_2CO_3 > KOH > Na_2CO_3 > NaOH$. Generally, the use of alkaline catalysts hinders the formation of char and favours the formation of oil products. However, the activity of alkaline catalysts appears to depend on the properties and type of biomass feedstock. Zhong and Wei (2004) performed direct liquefaction of different various types of woody biomass in hot-compressed water at 280–360°C. Heavy oil yields of 30 wt.% and residues of less than 10 wt.% were obtained for all the wood samples tested. However, their results showed that the addition of $K_2CO_3$ catalyst to feedstocks with lower lignin contents was less effective in producing oil products, although the catalyst reduced the residue yield for all the woods tested.

Acids were found to be less effective catalysts for high-pressure liquefaction of biomass, except in some liquefaction processes employing phenol. Zhang et al. (2006) investigated the liquefaction of powdered Chinese fir and poplar in phenol with the presence of a variety of inorganic acids: 85% phosphoric acid, 36% sulfuric acid, 37% hydrochloric acid and 99.5%

oxalic acid. The results showed that both phosphoric and sulfuric acid were effective in enhancing the liquefaction (phenolysis) efficiencies. It was found that an extremely low yield (<5 wt.%) of solid residue was obtained after 2 h liquefaction at 150°C when phosphoric or sulfuric acid was used.

Hot-compressed or sub-/supercritical water treatment has been studied by many researchers for biomass liquefaction (Xu and Donald, 2008; Xu and Lad, 2008; Adschiri et al., 1993; Sasaki et al., 2000; Saka and Ueno, 1999; Saka and Konishi, 2000; Matsumura et al., 1999). However, the drawbacks of using water as the solvent for liquefaction of coal or biomass include the following: lower yields of the water-insoluble oil product (with a greater heating value) compared to yields water-soluble product (with a lower heating value), and higher oxygen content in the liquefied products, resulting in low liquid product heating values (McDonald et al., 1983).

Recently, near-critical or supercritical fluids, compressed solvents above their critical temperature and pressure, have been investigated as solvents for the direct liquefaction of biomass. Supercritical fluids have the unique ability to dissolve materials not normally soluble in either a liquid or vapour phase and exhibit complete miscibility with the liquid and vapour products, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions (Savage, 1999; Demirbas, 2001). Sub-/super-critical water has been used for biomass liquefaction in many studies (Adschiri et al., 1993; Sasaki et al., 2000; Saka and Ueno, 1999; Saka and Konishi, 2000). Qian et al. (2007) investigated the liquefaction of woody biomass in water with an autoclave reactor operated at 280–420°C with sodium carbonate as the catalyst. They obtained a maximum yield of heavy oil of 53.3 wt.% at temperatures around 380°C.

Sub-/supercritical alcohols have been investigated as reaction media for the liquefaction of lignocellulosic materials in order to improve the yields of liquid oil products with a greater calorific value due to reduced oxygen contents (Xu and Etcheverry, 2008; Minami et al., 2003; Labreque et al., 1984; Poirier et al., 1987; Cemek and Kucuk, 2001; Ishikawa and Saka, 2001; Tsujino et al., 2003). Since alcohols have critical temperatures and pressures lower than those of water, much more moderate reaction conditions can be employed. Another advantage in using alcohols as reaction solvents for biomass liquefaction is that the alcohols are expected to readily dissolve relatively high molecular weight products derived from cellulose, hemicelluloses, and lignin due to their lower dielectric constants when compared with that of water (Yamazaki et al., 2006). In work by Xu and Etcheverry (2008) hydro-liquefaction of Jack pine powder was studied in sub-/supercritical ethanol with and without iron-based catalysts (5 wt.% FeS or $FeSO_4$). Very high liquid yields of 63 wt.% were obtained at 350°C for 40 min with the presence of $FeSO_4$ and 5.0 MPa cold pressure of $H_2$.

## 2.4 Bio-oil/Bio-crude Upgrading Processes

Biomass-derived oils are very different from crude oils obtained from petroleum sources; the sulfur and nitrogen content of bio-crudes is negligible, but they are rich in oxygen-containing molecules (see Table 2-2) (Georget et al., 1999). Bio-oils/bio-crudes are comprised of a complex mixture of oxygen-containing compounds in the form of phenol and benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols (Xu and Lad, 2008; Yang et al., 2009a). These compounds contribute to the oxygen content of the oil. In addition, water originating from both moisture initially present in the feedstock and as a pyrolytic product in pyrolysis and direct liquefaction processes adds to the oxygen content in bio-oil or bio-crude (Czernik and Bridgwater, 2004; Bridgwater, 2003). The total oxygen content of bio-crudes can be as high as 40-50 wt.% for pyrolysis oils, and 20-30 wt.% for heavy oils from high-pressure direct liquefaction process, depending on the origin of the biomass and liquefaction conditions, e.g. temperature, residence time, heating rate and different catalysts used (Furimsky, 2000; Bridgwater, 1994). The high oxygen content is a limitation in the utilization of bio-crude as liquid transportation fuel since the high oxygen content of the oils causes high viscosity, poor thermal and chemical stability, corrosivity (due to the organic acids present) and immiscibility with hydrocarbon fuels (Czernik and Bridgwater, 2004; Bridgwater, 2003; Yaman, 2004). Bio-crude/bio-oils therefore need to be upgraded by reducing their oxygen content (Bridgwater, 1994; Bridgwater, 1996).

Table 2-2 Elemental composition of bio-oil from wood and of a heavy fuel oil (Şenol, 2007).

| Composition (wt.%) | Bio-crude/Bio-oil | | Heavy Fuel Oil |
|---|---|---|---|
| | High-pressure liquefaction | Pyrolysis | |
| Carbon | 74.8 | 45.3 | 85.0 |
| Hydrogen | 8.0 | 7.5 | 11.0 |
| Oxygen | 16.6 | 46.9 | 1.0 |
| Nitrogen | <0.1 | <0.1 | 0.3 |
| Sulphur | <0.1 | <0.1 | 0.5-3.0 |
| HHV (MJ/kg) | ~30 | ~20 | ~40 |

Technologies for upgrading of bio-oils for fuel applications include physical and chemical/catalytic approaches (Zhang et al., 2007; Czernik et al., 2002). Techniques, such as emulsification and solvent extraction are physical methods in which bio-oils are mixed with diesel oil and solvents, respectively, to extract lower oxygen-containing components from the original bio-oil (Czernik et al., 2002). Although the physical mixing of bio-oils with diesel fuel directly, aided by the addition of a surfactant, may be the simplest way to use bio-oil as a liquid transportation fuel, the associated problem of corrosion to the engine and related components limits its application.

Currently, two main chemical approaches have been proposed and tested for the upgrading of both pyrolysis oils and bio-crudes from high-pressure direct liquefaction processes. These are catalytic cracking and catalytic hydro-treating and are analogous to the upgrading of heavy oils in a petroleum refinery.

Catalytic cracking processes, using various cracking catalysts (e.g. zeolites, silica–alumina and molecular sieves), are performed at atmospheric pressure without the requirement of added hydrogen. The advantages of low-pressure operation without the need of hydrogen have attracted much interest of studies on upgrading of bio-oils as reported in the literature (Adjave and Bakhshi, 1995; Katikaneni et al., 1995; Williams and Horne, 1995; Adjave et al., 1996). The yield of desired fuel hydrocarbons is however very low because of the high yields of char/coke and tar. Deposition of these undesired products on the catalyst results in the serious problem of rapid catalyst deactivation. As a result, periodic or continual regeneration of the catalysts becomes necessary.

In contrast to catalytic cracking, catalytic hydrotreating processes operate at high pressures in the presence of hydrogen and/or hydrogen donor solvents (Baker and Elliott, 1988; Craig and Coxworth, 1987; Maggi and Delmon, 1993). Significant efforts have been made over the past 20 years to study the hydrodeoxygenation (HDO) of biomass-derived oils.

The catalysts used in the hydro-treatment of bio-oils have been studied extensively and fall into two general categories: $Al_2O_3$-supported catalysts, typically loaded with NiMo or CoMo, (Baker and Elliott, 1988; Sharma and Bakshi, 1993; Sheu et al., 1988; Gevert et al., 1990) and zeolite catalysts (e.g. H-ZSM-5) (Baker and Elliott, 1988; Furrer and Bakshi, 1988; Sharma and Bakshi, 1991). The supported metal catalysts are more active in hydrogenation and deoxygenation reactions while the zeolite and similar acidic catalysts are used to enhance cracking reactions (Pindoria et al., 1998).

### *2.4.1 Hydro-treating of Model Compounds*

Review of research efforts to study the catalytic chemistry and kinetics of hydrotreating have focussed on various model compounds containing oxygen, such as phenolic compounds and aromatic ethers, as well as various bio-oils (fast pyrolysis oils and bio-crudes from high-pressure liquefaction processes) (Furimsky, 2000; Elliott 2007). Pacific Northwest National Laboratory (PNL/PNNL) employed a batch reactor to test hydro-treating of phenolic model compounds with various catalysts (Elliott, 1983). Some key results are summarized as follows: commercially available catalysts ($Al_2O_3$-supported CoMo, NiMo, NiW, Ni, Co, Pd, and CuCrO) were used to hydrogenate phenol at 300°C or 400°C for 1 h. Of the catalysts tested, the sulfided form of CoMo was found to be most active, producing a product containing 33.8% benzene and 3.6% cyclohexane at 400°C, while the sulfided Ni catalyst produced 8.0% cyclohexane but only 0.4% benzene. On the basis of other model compound studies involving o-cresol and naphthalene, Elliott, et al. (1995) concluded that NiMo with a phosphated alumina support was the most active for oxygen removal and hydrogen addition, but the authors pointed out that if hydrodeoxygenation is the main goal the CoMo catalyst shall be considered due to its much higher selectivity.

The addition of a small amount of phosphorus to sulfided $NiMo/Al_2O_3$ catalyst has been shown to enhance both hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) activities, with less susceptibility to coke formation (DeCanio et al., 1991). The presence of phosphorus was found to induce the formation of new Brönsted and Lewis acid sites with intermediate strength as was evidenced by FTIR analysis (Ferdous et al., 2004).

One of the key parameters determining the hydrodeoxygenation (HDO) activity of Mo, CoMo or NiMo catalysts is the type of support material used. The most common and conventional support is solid acid $Al_2O_3$, which has been widely used in hydro-treating catalysts on an industrial scale (Zdrazil, 2003). Extensive studies have been undertaken on CoMo and NiMo catalysts supported on alternative materials such as $SiO_2$, activated carbon, $TiO_2$, $ZrO_2$, zeolites and various mixed oxides (Breyesse et al., 1991; Luck, 1991; Topsøe et al., 1996; Vasudevan and Fierro, 1996; Radovic and Rodriguez-Reinoso, 1997). Centeno, et al. (1995) compared the HDO abilities with carbon-supported and alumina-supported CoMo and NiMo catalysts using various oxygen-containing and phenolic model compounds including guaiacol, catechol, phenol, 4-methyl acetophenone and *para*-cresol, in a *para*-xylene medium. Their studies showed that coke formation was an important cause of catalyst deactivation where alumina supports are used, especially with compounds containing two oxygens such as guaiacols or catechols.

The use of MgO as a basic support material has attracted much less attention. Basic supports however are interesting for two main reasons as stated by Klicpera and Zdrazil (2002). First, the acid–base interaction between acidic $MoO_3$ and a basic support in the oxide precursors of the sulfided catalyst may promote dispersion of the Mo species in the catalyst. Second, the basic character of the support may inhibit coking which is rather intensive for conventional $Al_2O_3$-supported catalysts. It was not until recently that MgO-supported catalysts have been used to upgrade bio-oil. Sulfided MgO-supported CoMoP catalyst was used to successfully upgrade both phenol (as a model compound) and bio-oil in supercritical hexane. After 1 h at optimum reaction conditions of 450°C and 5.0 MPa hydrogen, the phenol had been converted to reduced products comprising ~65 wt.% benzene and >10 wt.% cyclohexyl compounds (Yang et al., 2009b).

### *2.4.2 Hydro-treatment of Bio-oils*

Studies on the hydro-treatment of bio-oils have mostly focused on conventional petroleum hydrotreating catalysts, i.e., sulfided CoMo and NiMo. Elliott and Baker (1984) and Soltes et al. (1987) examined hydro-catalytic reactions of bio-oils obtained from a high-pressure liquefaction process using a continuously fed fixed bed reactors. Their results showed the sulfided form of the CoMo catalyst to be much more active than the oxide form. The sulfided nickel catalyst exhibited similar activity to the sulfided CoMo catalyst except that the nickel catalyst led to a much higher gas yield and much greater hydrogen consumption. More than 95% oxygen removal from the wood-derived bio-crude, initially containing about 15 wt.% O, was achieved with the sulfided CoMo/$Al_2O_3$ catalyst at 573 K (Gevert, 1988). Using the same bio-oil, Gevert et al. (1990) studied the effect of pore diameter of a sulfided CoMo/$Al_2O_3$ catalyst on the overall HDO. The best performance was achieved at 623 K for a catalyst with narrow pores. A two-step hydrotreatment process for upgrading of pyrolysis oils developed was developed at the PNNL (Elliott and Neuenschwander, 1996; Elliott et al., 1988; Elliot and Oosmaa, 1991). The first step involves a low temperature and high pressure (270°C, 136 atm) catalytic treatment that hydrogenates the thermally unstable bio-oil compounds. The second step involves catalytic hydrogenation at higher temperature and the same pressure (400 °C, 136 atm). The same catalyst, a sulfided CoMo/$Al_2O_3$ or sulfided NiMo/$Al_2O_3$, was used for both steps. This process produced 40 wt.% yields of refined oil containing less than 1 wt.% oxygen from a raw pyrolysis phenol (as a model compound) and bio-oil in supercritical hexane. After 1 h at optimum reaction conditions of 450°C and 5.0 MPa hydrogen, the phenol had been converted to reduced products comprising ~65 wt.% benzene and >10 wt.% cyclohexyl compounds (Yang et al., 2009b).

### *2.4.2 Hydro-treatment of Bio-oils*

Studies on the hydro-treatment of bio-oils have mostly focused on conventional petroleum hydrotreating catalysts, i.e., sulfided CoMo and NiMo. Elliott and Baker (1984) and Soltes et al. (1987) examined hydro-catalytic reactions of bio-oils obtained from a high-pressure liquefaction process using a continuously fed fixed bed reactors. Their results showed the sulfided form of the CoMo catalyst to be much more active than the oxide form. The sulfided nickel catalyst exhibited similar activity to the sulfided CoMo catalyst except that the nickel catalyst led to a much higher gas yield and much greater hydrogen consumption. More than 95% oxygen removal from the wood-derived bio-crude, initially containing about 15 wt.% O, was achieved with the sulfided CoMo/$Al_2O_3$ catalyst at 573 K (Gevert, 1988). Using the same bio-oil, Gevert et al. (1990) studied the effect of pore diameter of a sulfided CoMo/$Al_2O_3$ catalyst on the overall HDO. The best performance was achieved at 623 K for a catalyst with narrow pores. A two-step hydrotreatment process for upgrading of pyrolysis oils developed was developed at the PNNL (Elliott and Neuenschwander, 1996; Elliott et al., 1988; Elliot and Oosmaa, 1991). The first step involves a low temperature and high pressure (270°C, 136 atm) catalytic treatment that hydrogenates the thermally unstable bio-oil compounds. The second step involves catalytic hydrogenation at higher temperature and the same pressure (400 °C, 136 atm). The same catalyst, a sulfided CoMo/$Al_2O_3$ or sulfided NiMo/$Al_2O_3$, was used for both steps. This process produced 40 wt.% yields of refined oil containing less than 1 wt.% oxygen from a raw pyrolysis oil. Catalyst deactivation and gum formation in the lines were found to be the major process challenges. Churin et al. (1988 and 1989) conducted upgrading experiments on pyrolysis oil produced from olive oil. The authors reported that using sulfided NiMo or CoMo catalysts on alumina or silica-alumina supports perform better than noble metal catalysts which were found to be more readily deactivated by poisoning, sintering, and fouling. The use of a hydrogen donor solvent (e.g. tetrahydronaphthalene also known as tetralin) was found to lead to a marked improvement in the quality of the hydro-treated product and a reduction in catalyst deactivation by coke deposition. Zhang et al. (2005) hydrotreated a pyrolysis oil using sulfided CoMoP/$\gamma$-$Al_2O_3$, in tetralin under the optimum conditions of 360°C and 2 MPa of cold hydrogen pressure. The oxygen content of the oil was reduced from 41.8 wt.% for the crude oil to 3 wt.% for the upgraded product. A pyrolytic lignin, extracted from softwood fast pyrolysis bio-oil, was catalytic hydro-treated by Piskorz et al (1989) using pelletized sulfided CoMo catalyst. The process produced a light organic oil with 0.46% oxygen content.

Soltes et al. (1987) and Sheu et al. (1988) upgraded pyrolytic oils obtained from pine. Twenty catalyst formulations were tested in a batch reactor and an alumina-supported Pd catalyst was determined to be most effective with the highest yield of liquid oil at 400 °C for 1 h. Alumina-supported Pt or Re catalyst were found to produce higher gas yields, while Ru and Rh were found to be most active in gas formation. Sulfided CoMo, NiMo, and NiW catalysts were found to be of much lower activity for bio-oil hydro-treating compared to the precious metal catalysts, and the Pt catalyst was found to be the most active for oxygen removal.

Although sulfided CoMo and NiMo catalysts are traditionally used in petroleum and bio-oil hydro-treatment and have received much of the focus for HDO processes, other types of catalysts, including solid acids, solid bases and precious metal catalysts, have also been considered. Upgrading of fast pyrolysis oil using solid acid ($40SiO_2/TiO_2\text{-}SO_4^{2-}$) and solid base ($30K_2CO_3/Al_2O_3\text{-}NaOH$) catalysts at 50°C for 5 h was investigated by Zhang et al. (2006) in which the dynamic viscosity of the bio-oil was markedly decreased. The density of the upgraded bio-oil was decreased from 1,240 to 960 kg/$m^3$, and the gross calorific value increased by 50% from 16 MJ/kg for the original bio-oil to 24 MJ/kg for the upgraded bio-oil. The results of GC/MS analysis showed that de-carboxylation of the bio-oil was promoted by both the solid acid and solid base catalysts.

A longstanding problem for HDO of bio-oils was associated with catalyst deactivation due to coke formation, particularly for alumina-supported catalysts. Gagnon and Kaliaguine (1988) reported that bio-oil polymerization occurred during the upgrading of the vacuum pyrolysis bio-oil. The polymerization was more evident during bio-oil upgrading in the presence of $NiWO/Al_2O_3$ catalyst at 598 K and about 18 MPa $H_2$, although significant oxygen removal was achieved.

The development of highly active and stable catalysts for the HDO of bio-oils/ bio-crudes will continue to be the great challenge in the advancement of bio-oils and the focus of much future study.

## 2.5 Glycerol Utilization

Glycerol (1,2,3-propnaetriol) is a clear, viscous liquid that freezes at 17°C and boils at ~290°C. It is a byproduct of bio-diesel production (via trans-esterification) and is becoming increasingly available as the level of bio-diesel production worldwide increases. Approximately 1 kg of glycerol is produced for every 9 kg of bio-diesel that is produced (Dasari et al., 2005). The increasing demand for bio-diesel has produced a glut of glycerol which has in turn decreased the cost of crude (80%) glycerol from \$2.50/lb in 2004 to ~30¢/lb in 2006 (Yazdani and Gonzalez, 2007). Due to its growing availability and decreasing cost, much research is being conducted to try to make value-added products and bio-fuels from the glycerol obtained from biodiesel production instead of disposal by incineration.

### *2.5.1 Fuel Production from Glycerol*

The literature published on the conversion of glycerol into fuels can be divided into two basic processes: thermal conversion processes (i.e. pyrolysis, steam reforming and super-critical water reforming) and biological processes. Thermal conversion mainly aims to gasify glycerol feed into hydrogen or syn gas, which can be converted into liquid fuels by Fisher-Tropsch synthesis. Pyrolysis of glycerol is similar to the process used to produce pyrolysis oils from woody biomass however glycerol is pyrolized at much higher temperatures to promote conversion to gaseous products. Valliyappan et al. (2008) reported pyrolysis of glycerol at temperatures between 650–800°C, producing gas products, mostly syngas (CO, $H_2$) at concentrations ranging from 70–93 mol% in the gas products. The gas also contained $CH_4$ and $C_2H_4$ at concentrations of 3–15 mol% and 2–12 mol% respectively. Under the optimum condition of 800°C, a 72 wt.% glycerol stream was converted into 93.5 mol% syngas (of total gas produced) with a $H_2/CO$ of 1.05. Zhang et al. (2007) reported effective steam reforming of glycerol over ceria ($CeO_2$)-supported Ir, Co and Ni catalysts. The Ir catalyst proved to be more effective than the other metals tested and showed 100% glycerol conversion at 400°C with a hydrogen selectivity of more than 85%. Glycerol has also been converted in hydrogen over Ni/MgO catalyst (Adhikari et al., 2008). A maximum hydrogen yield of 56.5 mol%, with a selectivity of 65.6%, was obtained at 650 C with a 1:6 glycerol in water feed. Wen et al. (2008) found that aqueous phase reforming of glycerol over Pt catalyst at a lower temperature was also effective. They noted that hydrogen production was maximized over basic supports while alkane production was favoured over acidic support media. The zeolite-supported catalysts were found to be unstable under the chosen reaction conditions and collapsed. Steam reforming of glycerol over commercial Ni catalyst and a calcined dolomite sorbent at ambient pressure and moderate to high temperatures was reported by Dou et al. (2009). Hydrogen production was found to increase with increasing pressure and methane production was found to decrease to negligible levels at temperatures over 500°C. Byrd et al. (2008) reported effective glycerol reforming in supercritical water over alumina-supported Ru catalyst.

Biological processes for hydrogen production involve the use of anaerobic microorganisms to convert the glycerol into hydrogen and other gases through fermentation reactions (as opposed to aerobic reactions which result in $CO_2$ production). Sabourin-Provost and Hallenbeck (2009) showed that the photosynthetic bacterium *Rhodopseudomonas palustris* is capable of the photofermentative conversion of both pure and crude glycerol into hydrogen. They reported the production of 6 mol $H_2$/mol glycerol. Dark fermentation (as opposed to photofermentation) has also been used to produce hydrogen from glycerol (Chong et al., 2009).

Less frequently reported is the use of glycerol as a fuel for fuel cells. Glycerol is of interest due to its higher energy density than other fuels that have been used in fuel cells. Arechederra et al. (2007) reported the use of glycerol as a fuel for an enzymatic biofuel cell. The enzymes used oxidize the glycerol to mesoxalic acid via a multiple step process which makes use of 86% of the energy content of the glycerol. Room temperature reaction resulted in power densities up to $1.21 \mathrm{mW \cdot cm^{-2}}$. In addition, the glycerol does not swell the PEM (polymer electrolyte membrane) thereby allowing the use of highly concentrated (up to 98.9 wt.%) feed streams. PEM reactors have also been used to reform glycerol by means of electrolysis (Marshall and Haverkamp, 2008). The authors reported hydrogen gas yields of 10 $m^3$ $H_2 \cdot day^{-1} \cdot m^{-3}$ while using approximately 66% less energy than water electrolysis.

### *2.5.2 Chemical Production from Glycerol*

Glycerol is not suitable as an additive to gasoline and diesel by itself because it is practically insoluble in hydrocarbons. In addition it is water soluble and would increase fuel viscosity. (Gutierrez and Krause, 2008). It can however be converted or modified into compounds that can be added to hydrocarbon fuels to improve fuel performance.

One such process is acetlylation (esterification with acetic acid) of the glycerol to produce di- and tri-acetylglycerol which exhibits enhanced cold and viscosity properties when blended with diesel fuel and anti-knocking properties when added to gasoline (Melero et al., 2007). Melero et al. obtained over 90% conversion of glycerol with combined selectivity for di- and tri-acetyl-glycerol of over 85% after 4 h reaction with acetic acid over sulfonic acid-modified catalyst. The acid strength of catalytic sites was shown to be a determinant parameter in catalyst performance with stronger acid centers improving both glycerol conversion and selectivity toward the desired products.

It is also possible to produce ethers from glycerol. Typically this involves the reaction of glycerol with iso-butene or t-butyl alcohol to produce di- and tri-tertiary butyl ethers. Melero et al. (2008) reported complete glycerol conversion over sulfonic catalyst under optimized reaction conditions with a combined selectivity towards DTBG and TTBG up to ca. 90%. Klepacova et al. (2005) studied etherification of glycerol with isobutylene and tert-butyl alcohol, without solvent, over several catalysts. Glycerol conversion of 100%, with a selectivity for the desired products of ~89%, was obtained over a strong acid Amberlyst type ion-exchange resin at 60°C. Increased temperature (90°C) was found to decrease both glycerol conversion and yield of the desired products. Etherification with t-butyl alcohol was found not to be as effective due to the formation of water during the reaction and subsequent catalyst deactivation.

Being a polyalcohol itself, it is a small leap to see that glycerol could be the feedstock for the production of glycols and simple alcohols including propylene glycol, ethanol and butanol.

Propylene glycol is used in many of the same applications as ethylene glycol (such as antifreeze) but it is less toxic than the latter compound. Dasari et al. (2005) reported hydrogenolysis of glycerol to propylene glycol over copper-chromite catalyst. Mild conditions of 200°C and 200 psi over 24 h resulted in a maximum conversion of ~55% with a selectivity towards propylene glycol of almost 47% giving in a maximum yield of 85 wt.%. Zhang et al (2006) investigated propylene glycol production by anaerobic fermentation of glycerol by *K. pneumoniae*. Approximately 57 wt.% yield of 1,3-propylene glycol was observed. The formation of ethanol by the bacteria was found to hinder the production of the desired product. Selective dehydroxylation of glycerol by tosylation has been reported (Wang et al., 2003). The reaction involves guarding the terminal hydroxyl groups by acetalization and then converting the middle hydroxyl group into a tosyloxyl group. The tosyloxyl group is then removed by catalystic hydrogenolysis. This process is not economically viable, however, due to low (<15 wt.%) yields of propylene glycol. More favourable results have been achieved using Cu/MgO catalysts (Yuan et al., 2010). Up to 72% conversion and 97.6% selectivity were observed, giving an overall propylene glycol yield of 70.3 wt.%. The addition of a small amount of NaOH to the reaction mixture was found to increase glycerol conversion to 82%.

Yazdani and Gonzalez (2007) reported producing ethanol from glycerol via anaerobic fermentation using *E. coli.* Other microorganisms including *Klebsiella pneumoniae*, *Clostridium pasteurianum*, *Citrobacter freundii*, and *Enterobacter agglomerans* have also been investigated for the production of ethanol and other low alcohols (e.g. butanol) from glycerol (Menzel et al., 1997; Barbirato et al., 1998; Himmi et al., 1999; Nakamura and Whited, 2003; Biebel, 2001; Malinowski, 1999). Yazdani and Gonzalez (2007) also stated that anaerobic digestion of glycerol can produce other chemicals such as formates and succinates. Lee et al. (2001) produced succinic acid from glycerol using *Anaerobiospirillum succiniciproducens*.

Acrolein (propenal) is an important chemical intermediate that is used in the production of acrylic acid esters, superabsorber polymers and detergents. It is typically prepared by gas phase oxidation of propylene over Bi/Mo-mixed oxide catalyst. Vogel et al (2006) reported plug flow dehydration of glycerol into acrolein in sub- and supercritical water over zinc sulfate catalyst. Reaction conditions ranged from 300–390 °C, 25–34 MPa, and 10–60 s residence time. They achieved a maximum glycerol conversion of 50% at 360°C and 25 MPa with a selectivity of 75%. Higher yields and better selectivity have been reported by Watanabe et al. (2007), where glycerol was reacted in hot-compressed and supercritical water in both batch and flow reactors. A maximum conversion of 90% with 80% selectivity towards acrolein (72 wt.% yield) was achieved over acid-modified catalyst under supercritical conditions of 400°C and 34.5 MPa. Gas phase dehydration of aqueous glycerol to acrolein was investigated in a flow reactor by Jia et al. (2010). High Si/Al ratio nanocrystalline catalysts were compared to bulk catalysts and exhibited greatly enhanced performance even at very high GHSVs of 1438 $h^{-1}$. The most effective catalyst exhibited almost 100% conversion of the 35 wt.% glycerol feed even after 24 h on-line. Not unexpectedly, glycerol conversion was found to decrease with increased GHSV. Selectivity for acrolein, however, was found to increase with increased GHSV likely due to the shorter residence time which minimized possible side reactions. Corma et al. (2008), Zhou et al. (2007), Tsukuda et al. (2007), and Ning et al. (2008) have also investigated glycerol-to-acrolein conversion.

Although there is a large body of research investigating the use of the large surplus of glycerol produced by bio-diesel production, the research has mainly focussed on converting glycerol into fuel as hydrogen or syngas for subsequent F-T synthesis, using glycerol as a fuel itself or converting it into other chemicals such as propylene glycol, acrolein, oxygenates (esters and ethers) for use as fuel additives, and various alcohols. None of the research however, has reported the use of glycerol as a feedstock for the production of bio-crude oil. As discussed previously, in research by Dasari et al. (2005) for hydrogenolysis of glycerol to propylene glycol over copper-chromite catalyst, mild conditions were favorable for the yield and selectivity of the propylene glycol products. Higher temperatures and pressures were found to increase condensation reactions, leading to a greater oily product yield. By tuning the reaction conditions, conditions (type of catalysts, reaction temperature, reaction time, hydrogen pressure, and solvent effects), a high yield of bio-crude oil would be achievable via hydro-treatment of glycerol.

## 2.6 Summary

1) Fast pyrolysis is the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils contain high levels of oxygenated compounds and water, and therefore have lower caloric values than petroleum oils.

2) High-pressure liquefaction technology which uses moderate temperatures <400°C but higher pressures of 5-20 MPa has the potential to produce superior quality bio-oils with much higher caloric values (25-35 MJ/kg).

3) The bio-oils/bio-crudes produced by biomass liquefaction are composed of a complex mixture of oxygen-containing compounds in the form of phenol and benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols. The high oxygen content of the bio-oils limits their usefulness as liquid transportation fuels since the high oxygen content results in increased viscosity, poor thermal and chemical stability, corrosivity (due to the organic acids present) and immiscibility with hydrocarbon fuels. Pyrolysis oils/bio-crudes, therefore, need to be upgraded to reduce their oxygen content in order to convert them into useful fuels.

4) Catalytic cracking and catalytic hydro-treating are the two typical technologies used in the upgrading of bio-oils for fuel applications. Catalytic cracking processes, which use cracking catalysts (e.g. zeolites, silica–alumina and molecular sieves), are performed at atmospheric pressure without the requirement of additional hydrogen. In contrast, catalytic hydro-treating processes operate at higher pressures (2-20 MPa) in the presence of hydrogen and/or in the presence of hydrogen donor solvents.

5) Commercially available sulfided catalysts ($Al_2O_3$-supported CoMo, NiMo, NiW, Ni, Co, Pd, and CuCrO) have been widely used for hydrodeoxygenation (HDO) of both bio-oils and model compounds. Alumina-supported Pd catalysts have been found to be the most effective catalysts, producing higher bio-oil yields than conventional Mo-based catalysts. Catalyst deactivation due to the formation of coke and tars has been identified as the major issue with the conventional alumina-supported catalysts.

6) Glycerol is a potential feedstock for many fuels and value-added products that is rapidly becoming more accessible as the production of bio-diesel increases.

7) Current research into glycerol utilization has focussed on the production of syn-gas, pure hydrogen, and chemicals such as acrolein, epichlorohydrin, propylene glycol, various other alcohols and oxygenates to be used as fuel additives.

8) From the available literature however, no research has been reported on the hydrodeoxygenation of glycerol into bio-oil. By tuning the reaction conditions, conditions (type of catalysts, reaction temperature, reaction time, hydrogen pressure, and solvent effects), a high yield of bio-crude oil could be achievable via hydro-treatment of glycerol.

## References

Adhikari S, Fernando SD, Haryanto A. Hydrogen production from glycerin by steam reforming over nickel catalysts. *Renew Energy* **33** (2008) 1097–100.

Adjave JD, Bakhshi NN. Production of hydrocarbons by catalytic upgrading of a fast pyrolysis bio-oil. Part I: Conversion over various catalysts. *Fuel Process. Technol.* **45** (1995) 161-183.

Adjave JD, Katikaneni SPR, Bakhshi NN. Catalytic conversion of a biofuel to hydrocarbons: effect of mixtures of HZSM-5 and silica-alumina catalysts on product distribution. *Fuel Process. Technol.* **48** (1996) 115-143.

Adschiri T, Hirose S, Malaluan R, Arai K. Noncatalytic conversion of cellulose in supercritical and subcritical water. *J Chem Eng Jpn.* **26** (1993) 676-680.

Appel HR, Wender I, Miller RD. Conversion of urban refuse to oil. US Bureau of Mines, Technical Progress Report (1969) No. 25.

Appell HR, Fu YC, Friedman S, Yavorsky PM, Wender I. Converting organic wastes to oil. US Bureau of Mines, Report of Investigation (1971) No. 7560.

Appell HR. Fuels from waste. New York: Academic Press (1967).

Arechederra R, Treu BL, Minteer SD. Development of glycerol/$O_2$ biofuel cell, *Journal of Power Sources* **173** (2007) 156–161.

Baker EG, Elliott DC. Research in thermochemical biomass conversion. London: Elsevier Applied Science (1988) 883.

Barbirato F, Himmi EH, Conte T, Bories A. 1,3-Propanediol production by fermentation: an interesting way to valorize glycerin from the ester and ethanol industries. *Ind Crop Prod* **7** (1998) 281–9.

Biebl H. Fermentation of glycerol by Clostridium pasteurianum—batch and continuous culture studies. *J Ind Microbiol Biotechnol* **27** (2001) 18–26.

Boocock DGB, Mackay D, McPherson M, Nadeau S, Thurier R. Direct hydrogenation of hybrid poplar wood to liquid and gaseous fuels. *Can J Chem Eng* **57** (1979) 98-101.

Breysse M, Portefaix JL, Vrinat M. Support effects on hydrotreating catalysts. *Catal. Today* **10** (1991) 489-505.

Bridgwater AV, Bridge SA. Review of biomass pyrolysis processes. In Biomass Pyrolysis Liquids Upgrading and Utilisation; Elsevier: New York (1991) 11-92.

Bridgwater AV, Cottam ML. Opportunities for biomass pyrolysis liquids production and upgrading. *Energy Fuels* **6** (1992) 113-120.

Bridgwater AV, Czernik S, Piskorz, J. An overview of fast pyrolysis. Progress in thermochemical biomass conversion, Volume 2; Blackwell Science: London (2001) 977- 997.

Bridgwater AV. Catalysis in thermal biomass conversion. *Appl. Catal. A: Gen.* **116** (1994) 5-47.

Bridgwater AV. Production of high grade fuels and chemicals from catalytic pyrolysis of biomass. *Catal. Today* **29** (1996) 285-295.

Bridgwater AV. Renewable fuels and chemicals by thermal processing of biomass. *Chem. Eng. J.* **91** (2003) 87-102.

Byrd, AJ et al., Hydrogen productioon from glycerol by reforming in supercritical water over Ru/Al2O3 catalyst. *Fuel* **87** (2008) 2956-2960.

Cemek M, Kucuk MM. Liquid products from verbascum stalk by supercritical fluid extraction. *Energy Conversion Management* **42** (2001) 125-130.

Centeno A, Laurent E, Delmon B. Influence of the support of CoMo sulfide catalysts and of the addition of potassium and platinum on the catalytic performances for the hydrodeoxygenation of carbonyl, carboxyl, and guaiacol-type molecules. *J. Catal.* **154** (1995) 288-298.

Chong, M-L et al. Biohydrogen production from biomass and industrial wastes by dark fermentation. *Int. Journal of Hydrogen Energy* **34** (2009) 3277–3287.

Chornet E, Overend RP. Fundamentals of thermochemical biomass conversion. Amsterdam: Elsevier (1985).

Churin E, Grange P, Delmon B. Quality improvement of pyrolysis oils. Final report on contract no. EN3B-0097-B for the Directorate-General Science, Research and Development, Commission of the European Communities (1989).

Churin E, Maggi R, Grange P, Delmon B. Characterization and upgrading of a bio-oil produced by pyrolysis of biomass. Research in thermochemical biomass conversion, Elsevier Science Publishers, Ltd. (1988) 896-909.

Corma A, Huber GW, Sauvanaud L, O'Connor P. Biomass to chemicals: catalytic conversion of glycerol/water mixtures into acrolein, reaction network. *J Catal* **257** (2008) 163–71.

Craig W, Coxworth E. Proceedings of the sixth canadian bioenergy R&D seminar. London: Elsevier Applied Science (1987) 407.

Crofcheck C, Montross MD, Berkovich A, Andrews R. The effect of temperature on the mild solvent extraction of white and red oak. *Biomass Bioenergy* **28** (2005) 572-578.

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

Czernik S, Maggi R, Peacocke GVC. Review of methods for upgrading biomass-derived fast pyrolysis oils. Fast Pyrolysis of Biomass: A handbook (2002) 141-145.

Dasari, MA. et al., Low-pressure hydrogenolysis of glycerol to propylene glycol *Applied Catalysis A: General* **281** (2005) 225–231.

Decanio EC, Edwards JC, Scalzo TR, Storm DA, Bruno JW. FT-IR and solid-state NMR investigation of phosphorus promoted hydrotreating catalyst precursors. *J. Catal.* **132** (1991) 498-511.

Demirbas A. Conversion of biomass using glycerin to liquid fuel for blending gasoline as alternative engine fuel. *Energy Conversion Management* **41** (2000) 1741-1748.

Demirbas A. Mechanism of liquefaction and pyrolysis reactions of biomass. *Energy Conversion Management* **41** (2000) 633-646.

Demirbas A. Pyrolysis of ground beech wood in irregular heating rate conditions. *J. Anal. Appl. Pyrolysis* **73** (2005) 39-43.

Demirbas A. Supercritical fluid extraction and chemicals from biomass with supercritical fluids. *Energy Conversion Management* **42** (2001) 279-294.

Dou, B et al. Hydrogen production by sorption-enhanced steam reforming of glycerol *Bioresource Technology* **100** (2009) 3540–3547.

Elliott DC, Baker EG, Piskorz J, Scott DS, Solantausta Y. Production of liquid hydrocarbon fuels from peat. *Energy Fuels* 1988; 2: 234-235.

Elliott DC, Baker EG. Upgrading biomass liquefaction products through hydrodeoxygenation. *Biotechnol. Bioeng. Symp.* **14** (1984) 159-174.

Elliott DC, et al. Environmental impacts of thermochemical biomass conversion. NREL/TP-433-7867, National Renewable Energy Laboratory: Golden, Colorado (1995).

Elliott DC, Hart TR, Neuenschwander GG, McKinney MD, Norton MV, Abrams CW. Environmental impacts of thermochemical biomass conversion. NREL/TP-433-7867, National Renewable Energy Laboratory: Golden, Colorado (1995).

Elliott DC, Neuenschwander GG, Hart TR, Hu J, Solana AE, Cao C. Hydrogenation of bio-oil for chemical and fuel production. Science in Thermal and Chemical Biomass Conversion, CPL Press: Newbury Berks, UK (2006) 1536-1546.

Elliott DC, Neuenschwander GG. Developments in thermochemical biomass conversion. Blackie Academic and Professional: London (1996).

Elliott DC, Oasmaa A. Catalytic hydrotreating of black liquor oils. *Energy Fuels* **5** (1991) 102-109.

Elliott DC. Bench-scale research in biomass liquefaction by the CO-steam process. *Can. J. Chem. Eng.* **58** (1980) 730-734.

Elliott DC. Historical developments in hydroprocessing bio-oils. *Energy Fuels* **21** (2007) 1792-1815.

Elliott DC. Hydrodeoxygenation of phenolic components of wood-derived oil. *Am. Chem. Soc., Div. Pet. Chem.*, Prepr. **28** (1983) 185.

EU Directive 2003/30/EC, The promotion of the use of biofuels and other renewable fuels for transport., 8 May 2003.

Ferdous D, Dalai AK, Adjaye JD. A series of NiMo/Al2O3 catalysts containing boron and phosphorus Part I. synthesis and characterization. *Appl. Catal. A: Gen.* **260** (2004) 137-151.

Furimsky E. Review: catalytic hydrodeoxygenation. *Appl. Catal. A: Gen.* **199** (2000) 147-190.

Furrer RM and Bakhshi NN in Research in Thermochemical Biomass Conversion, eds A. V. Bridgewater and J. L. Kuester. Elsevier Applied Science, London and New York (1988) 956.

Gagnon J, Kaliaguine S. Catalytic hydrotreatment of vacuum pyrolysis oils from wood. *Ind. Eng. Chem. Res.* **27** (1988) 1783-1788.

Georget DMR, Cairns P, Smith AC, Waldron KW. Crystallinity of lyophilised carrot cell wall components. *Int. J. Biological Macromolecules* **26** (1999) 325-331.

Gevert SB, Andersson PBW, Sandqvist SP, Jaeraas SG, Tokarz MT. Hydroprocessing of directly liquefied biomass with large-pore catalysts. *Energy Fuels* **4** (1990) 78-81.

Gevert SB. Energy from biomass and wastes XI. IGT, Chicago (1988).

Gevert SB, Anderson BW and Sandqvist SP. Hydroprocessing of directly liquefied biomass with large-pore catalysts *Energy and Fuels* **4** (1990) 78-81.

Guo Y, Wang Y, Wei F. Research progress in biomass flash pyrolysis technology for liquids production. *Chem Ind Eng Progr* **8** (2001) 13-17.

Gutierrez A and Krause O, Production alternatives of biocomponents for diesel, Laboratory of Industrial Chemistry - TKK (2008).

Himmi EH, Bories A, Barbirato F. Nutrient requirements for glycerol conversion to 1,3-propanediol by Clostridium butyricum. *Bioresource Technol* 1999;67(2):123–8.

Ishikawa Y, Saka S. Chemical conversion of cellulose as treated in supercritical methanol. *Cellulose* **8** (2001) 189-195.

Jia C-J, Liu Y, Schmidt W, Lu A-H, Schüth F. Small-sized HZSM-5 zeolite as highly active catalyst for gas phase dehydration of glycerol to acrolein, *Journal of Catalysis* **269** (2010) 71–79.

Karagoz S, Bhaskar T, Muto A, Sakata Y, Oshiki T, Kishimoto T. Low-temperature catalytic hydrothermal treatment of wood biomass: analysis of liquid products. *Chem. Eng. J.* **108** (2005) 127-137.

Karagoz S, Bhaskar T, Muto A, Sakata Y. Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel* **83** (2004) 2293-2299.

Katikaneni SPR, Adjave JD, Bakhshi NN. Performance of aluminophosphate molecular sieve catalysts for the production of hydrocarbons from wood-derived and vegetable oils. *Energy Fuels* **9** (1995) 1065-1078.

Klepacova K, Mravec D, Bajus M, tert-Butylation of glycerol catalysed by ion-exchange resins, *Applied Catalysis A: General* **294** (2005) 141–147.

Klipcera T, Zdrazil M. Preparation of high activity MgO-supported Co-Mo and Ni-Mo sulfide hydrodesulfurization catalysts. *J. Catal.* **206** (2002) 314-320.

Labreque R, Kaliaquine S, Grandmaison JL. Supercritical gas extraction of wood with methanol. *Ind Eng Chem Prod RD* **23** (1984) 177-182.

Lee PC, Lee WG, Lee SY, Chang HN. Succinic acid production with reduced by-product formation in the fermentation of Anaerobiospirillum succiniciproducens using glycerol as a carbon source. *Biotechnol Bioeng* **72** (2001) 41–8.

Luck F. A review of support effects on the activity and selectivity of hydrotreating catalysts. *Bull. Soc. Chim. Belg.* **100** (1991) 781.

Maggi R, Delmon B. Advances in thermochemical biomass conversion. London: Elsevier Applied Science (1993) 1185.

Malinowski J. Evaluation of liquid extraction potentials for downstream separation of 1,3-propanediol. *Biotechnol Tech* **13** (1999) 127–30.

Marshall AT, Haverkamp RG, Production of hydrogen by the electrochemical reforming of glycerol-water solutions in a PEM electrolysis cell, *Int J Hydrogen Energy* **33** (2008) 4649–4654.

Matsumura Y, Nonaka H, Yokura H, Tsutsumi A, Yoshida K. Co-liquefaction of coal and cellulose in supercritical water. *Fuel* **78** (1999) 1049-1056.

McDonald EC, Howard J, Bennett B. Chemicals from forest products by supercritical fluid extraction. *Fluid Phase Equilibr.* **10** (1983) 337-344.

Melero JA, van Grieken R, Morales G, and Paniagua M, Acidic Mesoporous Silica for the Acetylation of Glycerol: Synthesis of Bioadditives to Petrol Fuel *Energy & Fuels* **21** (2007) 1782-1791.

Melero JA, Vicente G, Morales G, Paniagua M, Moreno JM, Roldán R, Ezquerro A, Pérez C. Acid-catalyzed etherification of bio-glycerol and isobutylene over sulfonic mesostructured silicas, *Applied Catalysis A: General* **346** (2008) 44-51.

Menzel K, Zeng AP, Deckwer WD. High concentration and productivity of 1,3-propanediol from continuous fermentation of glycerol by *Klebsiella pneumoniae*. *Enzyme Microb Technol* **20** (1997) 82–6.

Miller JE, Evans L, Littlewolf A, Trudell DE. Bath microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Fuel* **78** (1999) 1363-1366.

Minami E, Kawamoto H, Saka S. Reaction behaviors of lignin in supercritical methanol as studied with lignin model compounds. *J Wood Sci* **49** (2003) 158-165.

Minowa T, Kondo T, Sudirjo ST. Thermochemical liquefaction of Indonesia biomass residues. *Biomass Bioenergy* **14** (1998) 517-524.

Molten PM, et al. Mechanism of conversion of cellulose wastes to liquid in alkaline solution. *Energy from biomass and wastes III. Chicago, IL: Institute of Gas Technology* (1983) 293.

Nakamura CE, Whited GM. Metabolic engineering for the microbial production of 1,3-propanediol. *Curr Opin Biotechnol* **14** (2003) 454–9.

Ning L, Ding Y, Chen W, Gong L, Lin R, Lu Y, et al. Glycerol dehydration to acrolein over activated carbon-supported silicotungstic acids. *Chin J Catal* **29** (2008) 212–4.

Oasmaa A, Czernik S. Fuel oil quality of biomass pyrolysis oils-state of the art for the end users. *Energy Fuels* **13** (1999) 914-921.

Peng WM, Wu QY. Production of fuels from biomass by pyrolysis. *New Energy Sources* **22** (2000) 39-44.

Pindoria RV, Megaritis A, Herod A A and Kandiyoti R. A two-stage fixed-bed reactor for direct hydro-treatment of volatiles from the hydropyrolysis of biomass: effect of catalyst temperature, pressure and catalyst ageing time on product characteristics *Fuel* **77** (1998) 1715-1726.

Piskorz J, Majerski P, Radlein D, Scott DS. Conversion of lignins to hydrocarbon fuels. *Energy Fuels* **3** (1989) 723-726.

Poirier MG, Ahmed A, Grandmaison JL, Kaliaguine CF. Supercritical gas extraction of wood with methanol in a tubular reactor. *Ind Eng Chem Res* **26** (1987) 1738-1743.

Qian Y, Zuo C, Tan J, He J. Structural analysis of bio-oils from sub-and supercritical water liquefaction of woody biomass. *Energy* **32** (2007) 196-202.

Qu Y, Wei X, Zhong C. Experimental study on the direct liquefaction of Cunninghamia Lanceolata in water. *Energy* **28** (2003) 597-606.

Radovic LR, Rodriguez-Reinoso F. Carbon materials in catalysis. *Chem. Phys. Carbon* **25** (1997) 243-358.

Sabourin-Provost, G and Hallenbeck, PC High yield conversion of a crude glycerol fraction from biodiesel production to hydrogen by photofermentation. *Bioresource Technology* **100** (2009) (14), 3513–3517.

Saka S, Konishi R. Chemical conversion of biomass resources to useful chemicals and fuels by supercritical water treatment. In: Bridgwater A.V. (ed.), Progress in Thermochemical Biomass Conversion. Blackwell Science, Oxford, UK (2000) 1338–1348.

Saka S, Ueno T. Chemical conversion of various celluloses to glucose and its derivatives in supercritical water. *Cellulose* **6** (1999) 177-191.

Sakaki T, Shibata M, Sumi T, Yasuda S. Saccharification of cellulose using a hot-compressed water-flow reactor. *Ind Eng Chem Res.* **41** (2002) 661–665.

Sasaki M, Fang Z, Fukushima Y, Adschiri T, Arai K. Dissolution and hydrolysis of cellulose in subcritical and supercritical water. *Ind Eng Chem Res.* **39** (2000) 2883-2890.

Savage PE. Organic chemical reactions in supercritical water. *Chem. Review* **99** (1999) 603-621.

Schirmer RE, Pahl TR, Elliott DC. Analysis of a thermochemically-derived wood oil. *Fuel* **63** (1984) 368-372.

Scholze B, Meier D. Characterization of the water-insoluble fraction from pyrolysis oil (pyrolytic lignin) Part I. PY-GC/MS, FTIR, and functional groups. *J Anal Appl Pyrol* **60** (2001) 41-54

Şenol Oİ. Hydrodeoxygenation of aliphatic and aromatic oxygenates on sulphided catalysts for production of second generation biofuels. Helsinki University of Technology, (2007) ISBN 978-951-22-9035-2

Sharma RK, Bakhshi NN. Catalytic upgrading of biomass-derived oils to transportation fuels and chemical. *Can. J. Chem. Eng.* **69** (1991) 1071-1108.

Sharma RK, Bakhshi NN. Catalytic upgrading of pyrolysis oil. *Energy and Fuels* **7** (1993) 306-14.

Sheu YHE, Anthony RG, Soltes EJ. Kinetic studies of upgrading pine pyrolysis oil by hydrotreatment. *Fuel Process. Technol.* **19** (1988) 31-50.

Sipilae K, Kuoppala E, Fagernaes L. Characterization of biomass–based flash pyrolysis oils. *Biomass Bioenergy* **14** (1998) 103-113.

Soltes EJ, Lin SCK, Sheu YHE. Catalyst specificities in high pressure hydroprocessing of pyrolysis and gasification tars. Am. Chem. Soc., DiV. *Fuel Chem.* **32** (1987) 229-239.

Topsøe H, Clausen BS, Massoth FE. Hydrotreating catalysis, science and technology. Springer, Berlin (1996) pp. 1-24, 141-144, 310.

Tsujino J, Kawamoto H, Saka S. Reactivity of lignin in supercritical methanol studied with various lignin model compounds. *Wood Sci Technol.* **37** (2003) 299-307.

Tsukuda E, Sato S, Takahashi R, Sodesawa T. Production of acrolein from glycerol over silica-supported heteropoly acids. *Catal Commun* **8** (2007) 1349–53.

Valliyappan T, Bakhshi NN, Dalai AK, Pyrolysis of glycerol for the production of hydrogen or syn gas, *Bioresource Technology* **99** (2008) 4476–4483.

Vasudevan PT, Fierro JLG. A review of deep hydrodesulfurization catalysis. *Catal.Rev.* **38** (1996) 161-188.

Vogel H, Ott L, and Bicker M, Catalytic dehydration of glycerol in sub- and supercritical water: a new chemical process for acrolein production, *Green Chem.* **8** (2006) 214–220.

Wang K, Hawley MC, DeAthos SJ. Conversion of glycerol to 1,3-propanediol via selective dehydroxylation. *Ind Eng Chem Res* **42** (2003) 2913–23.

Watanabe M, Iida T, Aizawa Y, Aida TM, Inomata H, Acrolein synthesis from glycerol in hot-compressed water, *Bioresource Technology* **98** (2007) 1285–1290.

Wen, G et al. Production of hydrogen by aqueous-phase reforming of glycerol, *Intl J. of Hydrogen Energy* **33** (2008) 6657-6666.

Williams PT, Horne PA. The influence of catalyst regeneration on the composition of zeolite-upgraded biomass pyrolysis oils. *Fuel* **74** (1995) 1839-1851.

Xu C, Donald J. Upgrading peat to gas and liquid fuels in supercritical water with catalysts, *Fuel*: doi:10.1016/j.fuel.2008.04.042

Xu C, Etcheverry T. Hydro-liquefaction of woody biomass in sub- and supercritical ethanol with iron-based catalysts. *Fuel* **87** (2008) 335-345.

Xu C, Lad N. Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub/near-critical water. *Energy Fuels* **22** (2008) 635-642.

Yaman S. Pyrolysis of biomass fuels and chemical feedstocks. *Energy Convers.Manage.* **45** (2004) 651-671.

Yang Y, Gilbert A, Xu C. Production of bio-crude from forestry waste by hydro-liquefaction in sub-/super-critical methanol. *AIChE J.* **55** (2009)a 807-819

Yang Y, Gilbert A, Xu C Hydrodeoxygenation of bio-crude in supercritical hexane with sulfided CoMo and CoMoP catalysts supported on MgO: A model compound study using phenol *Applied Catalysis A: General* **360** (2009)b 242-249.

Yokoyama S, Ogi T, Koguchi K, Nakamura E. Direct liquefaction of wood by catalyst and water. *Liquid Fuels Technol* **2** (1984) 115-163.

Yuan Z, Wang J, Wang L, Xie W, Chen P, Hou Z, Zheng X. Biodiesel-derived glycerol hydrogenolysis to 1,2-propanediol on Cu/MgO catalysts *Bioresource Technology* **101** (2010) 7088-7092.

Zdražil M. MgO-supported Mo, CoMo and NiMo sulfide hydrotreating catalysts. *Catal. Today* **86** (2003) 151-171.

Zhang B, Tang X, Li Y, Xu Y, Shen W. Hydrogen production from steam reforming of ethanol and glycerol over ceria-supported metal catalysts. *Int J Hydrogen Energy* **32** (2007) 2367–73.

Zhang Q et al. Review of biomass pyrolysis oil properties and upgrading research. *Energy Conversion Management* **48** (2007) 87-92.

Zhang Q, Chang J, Wang T, Xu Y. Upgrading bio-oil over different solid catalysts. *Energy Fuels* **20** (2006) 2717-2720.

Zhang Q, Zhao G, Chen J. Effects of inorganic acid catalysts on liquefaction of wood in phenol. *Front. For. China* **2** (2006) 214-218.

Zhang SP, Yan YJ, Li T, Ren Z. Upgrading of liquid fuel from the pyrolysis of biomass. *Bioresour. Technol.* **96** (2005) 545-550.

Zhang SP, Yan YJ, Ren ZW. Analysis of liquid product obtained by the fast pyrolysis of biomass. *J Chin Sci Technol* **27** (2001) 666-668.

Zhang,Y et al. Glycerol fermentation by *Klepsiella pneumonia*. *Metabolic Engineering* **8** (2006) 578–586.

Zhong C, Wei X. A comparative experimental study on the liquefaction of wood. *Energy* **29** (2004) 1731-1741.

Zhou C-J, Huang C-J, Zhang W-G, Zhai H-S, Wu H-L, Chao Z-S. Synthesis of micro- and mesoporous ZSM-5 composites and their catalytic application in glycerol dehydration to acrolein. *Stud Surf Sci Catal* (2007) 527–30.

# CHAPTER 3

## Hydrodeoxygenation of Glycerol into Bio-crude: Catalyst Screening

Hydrodeoxygenation (HDO) of glycerol feedstock in the presence of various catalysts was investigated using a micro-reactor at a temperature of 300°C and initial hydrogen pressure of 5.0 MPa. The liquid products were separated into water-soluble components and bio-oil by liquid-liquid extraction with water and ethyl acetate. Without catalyst metals, the yields of bio-oil were in the range of 0.5 to 3.7 wt.%. The exception to this was the acidified zeolite which resulted in a bio-oil yield of ~34 wt.% but much greater char deposition. Various metals and combinations of metals were tested in an oxidized form and the most effective catalyst for glycerol HDO was found to be MoCoP/zeolite which resulted in an average bio-oil yield of ~39 wt.%. Glycerol gasification and hydrogen consumption were generally found to increase in proportion with increased bio-oil yields. Reduction and sulfidation of the MoCoP/zeolite catalyst was found to drastically reduce bio-oil yield and decrease hydrogen consumption. According to GC/MS analysis, the bio-oil products consist primarily of substituted phenols, ketones and substituted cyclic hydrocarbons in the C6 to C9 range. The bio-oils therefore contained a higher concentration of carbon and much lower concentration of oxygen than the original glycerol which resulted in a significantly increased heating value of 33 MJ/kg.

*Keywords:* bio-oil, bio-crude, glycerol, hydrodeoxygenation, catalysts

## 3.1 Introduction

In the past century, the world's energy demand has been met primarily by fossil fuels, comprising: 30% petroleum, 23% natural gas, 22% coal, 6% nuclear, and 19% renewable (Song, 2002). The era of fossil-resources-based energy and chemical industries is expected to phase out gradually over the course of the 21st century because of the depletion of fossil resources (Okkerse and Van Bekkum, 1999). Due to increasing concerns over greenhouse gas emissions and energy security, there has been a resurgence of interest in renewable bio-energy. Many countries have legislation in place to promote the use of biomass energy and bio-fuels. For example, the European Union has set an objective to increase the market share of biomass-derived fuels in the transport sector to 5.75% by the end of 2010 (EU Directive 2003/30/EC). In December 2007, then US President Bush signed into law a Renewable Fuels Standard (RFS) that calls for at least 36 billion gallons of ethanol and other bio-fuels to be used nationwide by 2022, including a minimum of 9 billion gallons in 2008, and 20.5 billion gallons by 2015 or about 15% replacement of the US's gasoline consumption. Concurrent with these initiatives, has been the increased production of bio-diesel from a variety of sources. Trans-esterification of fresh and spent cooking oils is one of the most common processes used to produce bio-diesel. The main by-product of trans-esterification is glycerol (approximately 1 kg of glycerol for every 9 kg of bio-diesel produced) (Dasari et al., 2005). The increased demand for bio-diesel has created a glut of glycerol (100,000 tonnes annually in the USA alone) and the cost of glycerol has decreased to a tenth of what it was just a few years ago (Yazdani and Gonzalez, 2007). Economically beneficial utilization of this glycerol by-product would greatly enhance biodiesel plant production economics. Much research is being conducted into the conversion of surplus glycerol into hydrogen (Marshal and Haverkamp, 2008, Valliyappan et al., 2005) and other value-added chemicals including ethanol (Yazdani and Gonzalez, 2007) and propylene glycol (Dasari et al., 2005, Zhang et al., 2008).

Glycerol, as an oxygenated organic compound, can be a promising feedstock for the production of liquid transportation fuels by oligomerization and de-oxygenation. However, there is no research available in published literature. This research investigated the effectiveness of different metal catalysts in the conversion of glycerol into bio-oil/bio-crude through a novel one-step hydrodeoxygenation (HDO) process under a hydrogen atmosphere. The catalysts tested were in an oxidized, reduced or sulfided form, and supported on MgO, activated carbon (AC), $Al_2O_3$ or zeolite materials.

## 3.2 Experimental

### *3.2.1 Feedstock and Catalyst Preparation and Characterization*

The feedstock for these experiments was reagent grade glycerol obtained from Canadawide Scientific (99% purity) and was used as received. The supported metal catalysts: 10% Co, Ni, Ru, or Mo as single metals, 10%Mo-3%Co, and 10%Mo-3%Co-2%P (MoCo and MoCoP for convenience) were synthesized by successive incipient wetness impregnation. The catalyst support materials (MgO, $\gamma$-$Al_2O_3$, activated carbon and X-type zeolite) were reagent grade and dried at 105°C in air for a minimum of 8 h before use. The metal salts (ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), ruthenium (III) nitrosylnitrate ($RuNO(NO_3)_3$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), and the phosphorous promoter (86 wt.% phosphoric acid) were A.C.S. reagent grade reagents obtained from Sigma-Aldrich and used as received. Briefly, approximately 10 or 20 g of support material was weighed into a flask. The required amount of metal compound was weighed into a separate beaker and dissolved in distilled water. The resulting mixture of the metal salt solution and the support solids was agitated in a shaker for a minimum of 6 h. After agitation, the water was removed by rotary evaporation at 85°C. The dewatered material was dried at 105°C for a minimum 12 h in air. Where additional catalyst metals were required, the dried catalyst was crushed into a fine powder with a mortar and pestle and the above procedure was repeated for each subsequent metal. After the final drying step, the impregnated metal catalysts were calcined at 550°C in air for 6 h. The cooled catalysts were crushed to a small (<200 μm) particle size before storage. The bulk elemental composition (molybdenum, cobalt and phosphorus contents) of selected catalysts were analyzed by inductively-coupled plasma-atomic emission spectroscopy (ICP-AES). These catalysts were also analyzed by X-ray diffraction (XRD) in order to determine their crystalline structures. The elemental analysis of these catalysts is presented in Table 3-1. Reduction of selected catalysts was performed in a flow reactor at 450°C under a hydrogen atmosphere for 4 h followed by passivation under a nitrogen atmosphere. Sulfidation of selected

Table 3-1. Elemental analysis of selected catalysts by ICP-AES and CNS

| **Catalyst** | **Mo** | **Co** | **P** | **Mg**[1] | **S** |
|---|---|---|---|---|---|
| | (10 wt.%) | (3 wt.%) | (1.5 wt.%) | (1.5 wt.%) | |
| MoCo/MgO | 7.8 | 2.4 | | | |
| MoCoP/MgO | 7.8 | 2.3 | 1.5 | | |
| MoCoP/Zeolite | 6.5 | 2.3 | 1.5 | | |
| MoCoP(R)/Zeolite | 6.5 | 2.3 | 1.5 | | |
| MoCoP(S)/Zeolite | 6.5 | 2.3 | 1.5 | | 5.6 |
| MoCoP/$Al_2O_3$ | 8.1 | 2.6 | 1.6 | | |
| MoCoP(R)/$Al_2O_3$ | 8.1 | 2.6 | 1.6 | | |
| MoCoP+Mg/$Al_2O_3$ | 8.0 | 2.6 | 1.6 | 1.2 | |

[1] Mg was added as an promoter by successive incipient wetness impregnation using $Mg(NO_3)_2$ solution

catalysts was performed with $CS_2$ in tetralin solvent at 400°C for 4 h under 7 MPa hydrogen in an autoclave reactor. The ratio of S to catalyst was 2:1 (w/w) and the tetralin solvent was present at 8:1 (w/w) in relation to the catalyst (adapted from Olson 1992). The sulfur content of the sulfided catalyst and the corresponding bio-oil product was determined by CNS.

As expected, the XRD spectrum of the MoCoP/zeolite catalysts (Figure 3-1) reveals multiple strong peaks that can be ascribed to crystallographic planes of the zeolite support. It is not a surprise to note that no XRD signals attributed to Co-containing species are visible due to its low content (<3 wt%, as displayed in Table 3-1). Four weak signals of $MoO_3$ were observed in the spectrum at $2\Theta$ = 12.5°, 26.5°, 36° and 53° (Patil et al., 2008). The peak at $2\Theta$ = 12.5° coincides with one of the crystallographic planes of the zeolite support. The $MoO_3$ peaks are

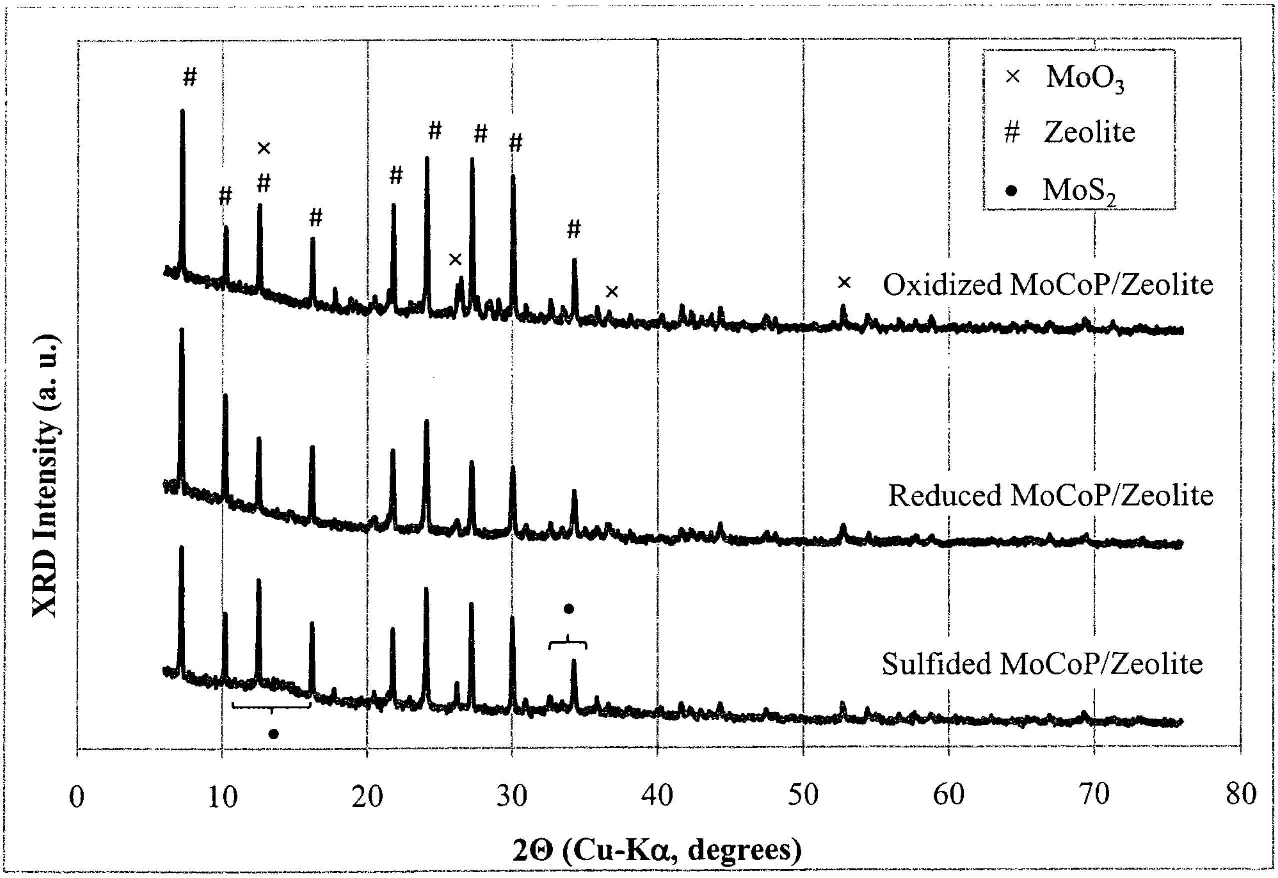


Figure 3-1. XRD spectra of MoCoP/zeolite catalyst in different chemical states

much lower in intensity compared to those of the zeolite due to the smaller amount of Mo present relative to the zeolite support. The lack of strong metal oxide signals may also imply that the metal species in these catalyst samples are highly dispersed (Byambajav and Ohtsuka, 2003, Radovic et al., 1983). Reduction of the MoCoP/zeolite catalyst resulted in a reduced signal from $MoO_3$ indicating that the oxide form was converted into its reduced form. However, no XRD lines ascribable to Mo metal were detected, probably due to the high dispersion or fine crystalline size (finer than 5 nm) of the metal species in the reduced catalyst (Byambajav and Ohtsuka, 2003, Radovic et al., 1983). Sulfidation of the MoCoP/zeolite catalyst resulted in reduced signals from the $MoO_3$ peaks. Instead two broad shoulders between $2\Theta = 12 - 16°$ and $32 - 35°$ became evident, which may ascribed to the diffraction of $MoS_2$ (Iwata et al., 1998).

The XRD spectra of the acidified zeolite and acidified zeolite-supported MoCoP catalyst are presented in Figure 3-2 along with the XRD spectrum of the MoCoP/zeolite catalyst for comparison. Unexpectedly, the acid appears to have partially destroyed the zeolite crystal structure as evidenced by the significant weakening of the signals due to zeolite. Most obvious are in the figure are very strong peaks that were identified by the X'Pert HighScore Plus software as being due to the presence of NaCl. The presence of NaCl in the acidified zeolite catalyst is not unexpected since there is Na present in the zeolite and it is available to react with the HCl that was used in the acidification process. The loading of metals onto the acidified zeolite reduced the amount of salt present in the catalyst according to the XRD spectrum, while diffraction lines of $\beta$-$MoCl_2$ were detected at $2\Theta = \sim13°$ which again may be due to the residual chloride in the acidified zeolite. A small amount of $MoO_3$ appears to be present as well. The peak labelled as "•" has not been definitively identified but several potential candidate compounds have been found including $Al(PO_4)$, $\varepsilon$-$MoO_3$, and $SiO_2$.

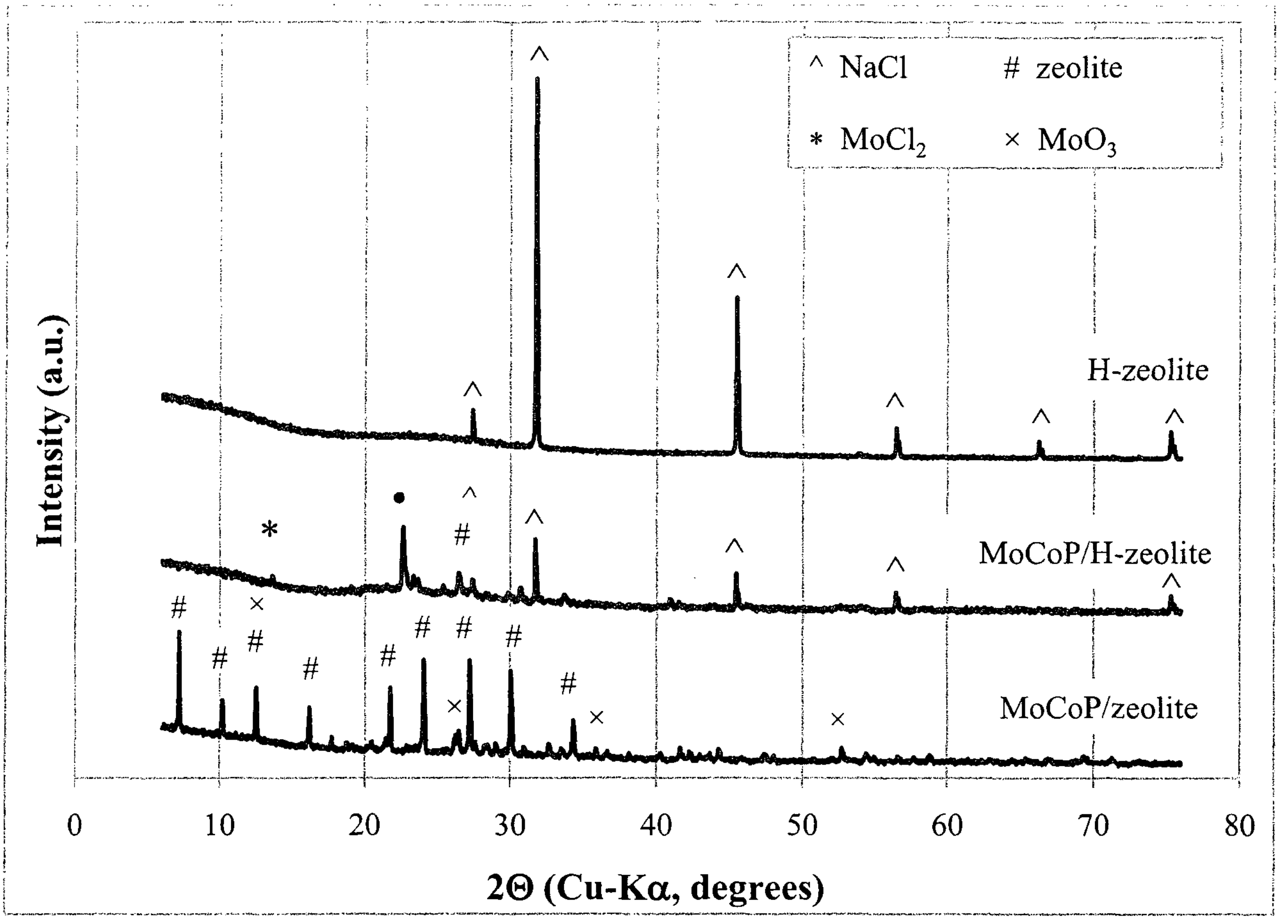


Figure 3-2. XRD spectra of H-zeolite and MoCoP/H-zeolite catalyst

The textural structure of several catalysts was analyzed by isothermal $N_2$ adsorption. The analyses of this catalyst are presented in Table 3-2.

Table 3-2. Elemental and textural analyses of several catalysts

| Catalyst | BET surface area ($m^2/g$) | Porosity (cc/g) | Average pore size (nm) |
|---|---|---|---|
| Zeolite | 3.1 | $8.89\times10^{-3}$ | 6.19 |
| H-zeolite | 67.3 | $4.96\times10^{-2}$ | 1.47 |
| MoCoP/H-zeolite | 2.9 | $1.44\times10^{-2}$ | 9.84 |
| MoCoP/zeolite | 2.6 | $1.29\times10^{-2}$ | 10.1 |
| MoCoP/zeolite (S) | 18.2 | $3.12\times10^{-2}$ | 3.43 |

### *3.2.2 Experimental Apparatus and Procedure*

The hydrodeoxygenation experiments were carried out in a micro-reactor made of stainless steel (SS 316L), consisting of capped 5/8 inch Swagelok bulkhead unions, with an effective volume of 14 mL. A schematic of the apparatus can be seen in Figure 3-3. In a typical run, 10 g of glycerol was weighed into the reactor, followed by the addition of catalyst (if needed) at a ratio of 5 wt.% of the glycerol. This ratio was chosen based on previous work done in the author's laboratory. The reactor was then securely sealed. The air in the reactor was displaced with high purity nitrogen by repetitive evacuation and $N_2$ purging. Finally, the reactor was pressurized to 5.0 MPa using high purity hydrogen. Supported on a mechanical shaker set at 100 rpm, the reactor was then rapidly heated in a fluidized sand bath to the specified

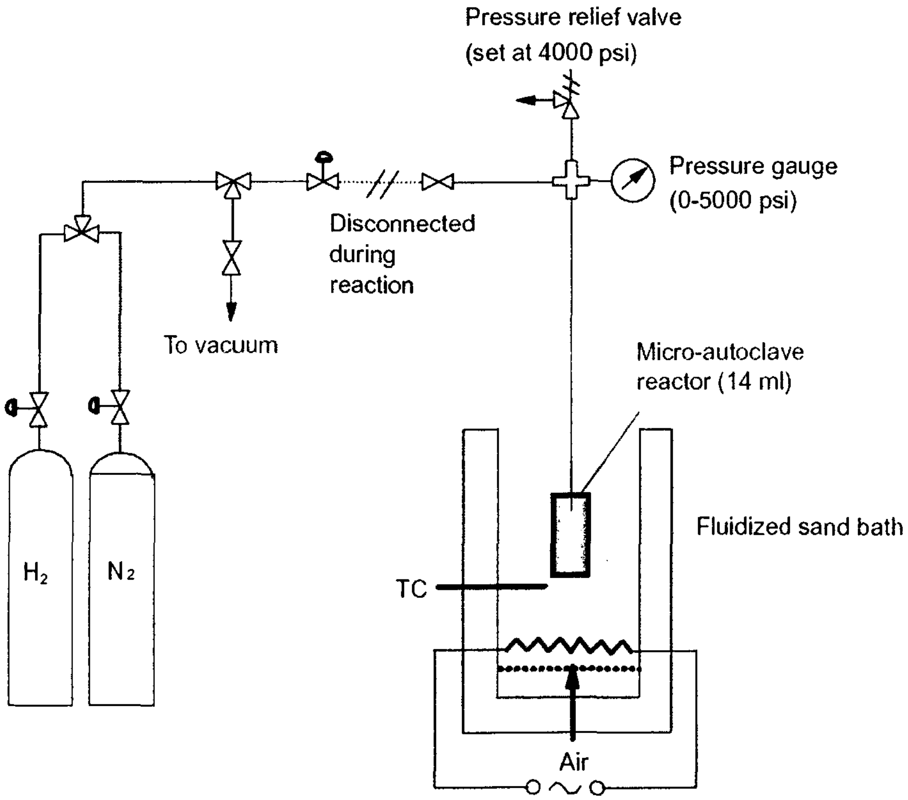


Figure 3-3. Schematic diagram of the micro-reactor apparatus

temperature of 300°C. After the standard reaction time of 1 h had elapsed, the reactor was removed from the sand bath and submerged in a water bath to terminate the reaction. A minimum of two runs were performed for each condition to ensure the reproducibility of the results, and that the errors between the results from the duplicate runs were all within 5% of one another.

### *3.2.3 Product Separation*

A scheme of the product separation process can be seen in Figure 3-4. Once the reactor had cooled to ambient temperature, the gaseous products were collected in a pre-evacuated sample cylinder with a fixed volume of 2.81 L. Cylinder pressure was brought to ambient pressure (required for analysis) by addition of high purity $N_2$. Gas composition was then analyzed by GC-TCD (Agilent 3000 Micro-GC). The total amount of gaseous product comprising CO, $CO_2$, and $C_1 - C_3$ hydrocarbon species, denoted as "gas" hereafter, was quantified. The solid/liquid products were rinsed completely from the micro-reactor with reagent grade ethyl acetate and distilled water. The resulting suspension was then filtered under vacuum through a pre-weighed Whatman No. 5 paper filter. The solids recovered in the filter paper consisted of char, ethyl acetate-insoluble residuum derived from glycerol during the reaction, and spent catalyst. The recovered solids were dried in an oven at 105°C overnight and allowed to cool in a desiccator before weighing. The filtrate was decanted from the filter flask into a separatory funnel. The filter flask was rinsed three times with ethyl acetate to ensure all oils were recovered. The filtrate was allowed to separate into two phases overnight. After separation samples of the organic layer were taken for GC/MS analysis. The aqueous layer was then decanted into a volumetric flask and diluted to a known volume with distilled water. Samples of the diluted aqueous phase were kept

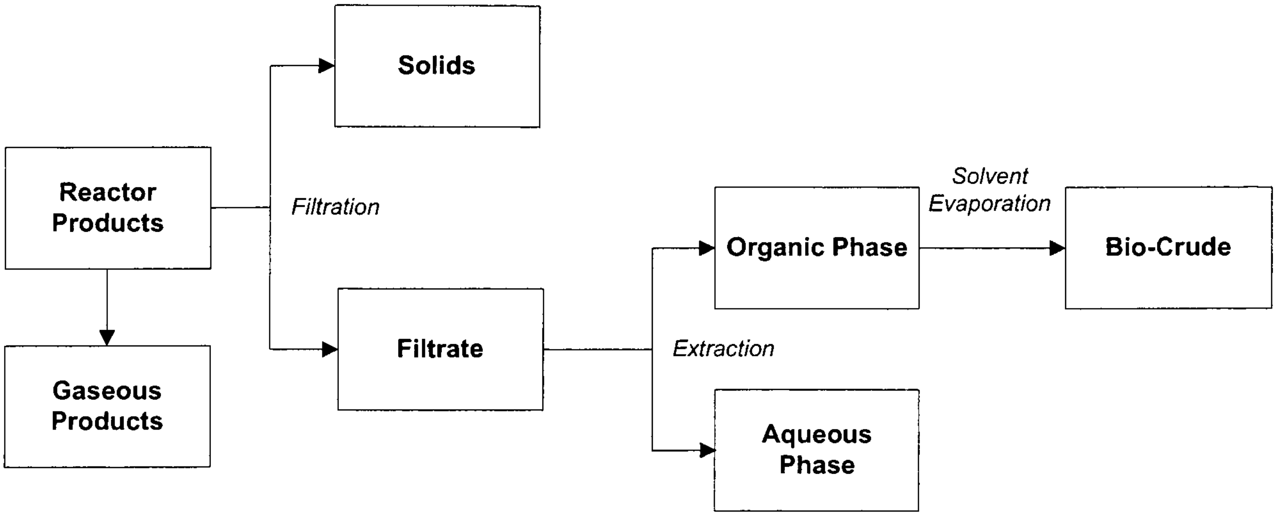


Figure 3-4. Product separation scheme

for DOC and HPLC analysis. The remaining organic liquid was rinsed into a pre-weighed round-bottomed flask and evaporated under vacuum at 60°C to remove the ethyl acetate. After evaporation, the flask was cooled in a desiccator and weighed to determine bio-oil yield. Where there was sufficient product yield, the viscosity of the bio-oil was measured with a Brookfield viscosimeter at 100 rpm and 50°C. The remaining bio-oil sample was then collected for later CHN analysis by dissolving in reagent grade acetone and stored at 4°C to minimize condensation/polymerization reactions. The yields of bio-oil, gaseous products, unreacted glycerol and char (solid residues), all expressed in wt.%, were calculated relative to the mass of glycerol feedstock fed into the reactor before the experiments.

### *3.2.4 Product Analysis*

As mentioned previously, the composition of the gaseous products was determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. These values were used to determine the mass of gaseous products produced. This mass was related to the mass of the glycerol feed and reported as the yield of gaseous products on a weight/weight basis. The elemental composition (C, H and N) of the bio-oil was determined with a CEC (SCP) 240-XA elemental analyzer. The oxygen content was estimated by mass difference, assuming negligible content of sulfur in the products. The lone exception to this was the bio-oil produced by the sulfided MoCoP/zeolite catalyst which was analyzed for S content. The bio-oil products were also analyzed by GC/MS (Shimadzu QP2010S) with a SHRXI- 5MS column (30 m×0.25 mm×0.25 μm) and a temperature program of initial oven temperature 40°C, 10°C/min ramp to 200°C, hold for 2 min. Longer runs did not produce an improvement in the data. The glycerol content of the aqueous phases was determined by HPLC (Waters Breeze with a 1525 binary HPLC pump and 2414 RI detector. The Bio-rad Aminex HPX-87H column was maintained at 65°C using 0.005M $H_2SO_4$ in water as the eluent at a flow rate of 0.6 mL/min. The dispersion states and chemical composition of certain catalysts before and after reaction were determined by X-ray diffraction (XRD) on a PANalytical X'Pert PRO X-ray diffractometer using Cu Kα radiation with a wavelength of 1.54187 Å.

### 3.3 Results and Discussion

The results of these experiments show that glycerol can be successfully dehydrated, deoxygenated, and oligomerized into bio-crude/bio-oil under hydrogen atmosphere with suitable catalysts. The yield of bio-oil was very high (up to ~40 wt%) in the presence of MoCoP catalyst. The yield of char/heavy residue was found to be negligible for nearly all of the catalysts tested. It should be noted here that the hydrogen was present in less-than-stoichiometric quantities relative to the glycerol and was therefore the limiting reagent in the reaction. Even so, in none of the runs was all of the hydrogen consumed, indicating that there is room for significant improvement in terms of product hydrogenation. This may be due to catalyst deactivation as will be discussed later. Testing at stoichiometric or greater-than-stoichiometric ratios was not possible due to the maximum pressure limitations in the reactor used for testing.

The theoretical maximum yield of product, assuming complete deoxygenation of the glycerol feed, is 47.8 wt.%. This is based on the difference in molecular weight between the glycerol feed (92 g/mol) and the deoxygenated product (44 g/mol for propane). Thus, 44/92 × 100% = 47.8 wt.%. This value will decrease if the propane polymerizes to produce alkanes or alkenes.

### *3.3.1 Effect of Catalyst Support Material*

The results of the hydrodeoxygenation tests on the four chosen support materials, including MgO, activated carbon (AC), $\gamma$-$Al_2O_3$ and an X-type zeolite are summarized in Figure 3-5.

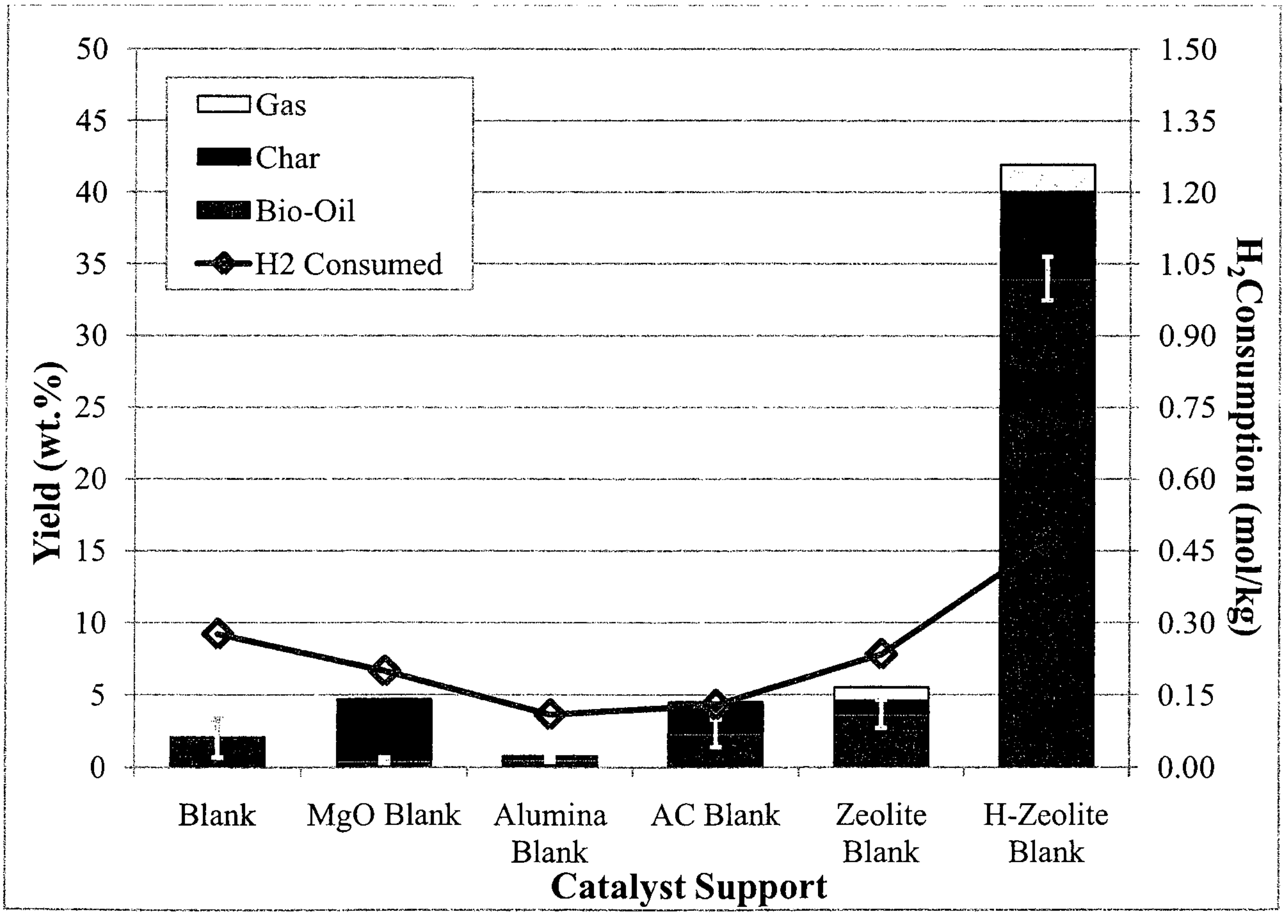


Figure 3-5. Effect of catalyst support material on product yields and $H_2$ consumption (300°C, 60 min).

These materials were chosen based on previous work done in the author's laboratory and are presented in comparison with a blank run performed without any catalyst or support material. The blank test produced a bio-oil yield of ~2.0 wt.%. The yield of bio-oil for the four support materials was negligible, ranging from 0.5 wt.% for MgO to a maximum of 3.7 wt.% for zeolite. The error bars represent a range of one standard deviation from the mean for the individual bio-oil yields. The means and standard deviations are the result of a minimum of two replicate runs. Hydrogen consumption was also minimal, ranging from a low of 0.11 mol/kg of glycerol for $Al_2O_3$ to a maximum of 0.23 mol/kg for zeolite. Gasification of glycerol, i.e. conversion of glycerol into gaseous products, was found to be negligible but generally increased with increasing bio-oil yield. This result was not unexpected since the cracking reactions that occur at elevated temperatures can produce molecular fragments that do not condense into either bio-oil or char but react with hydrogen atmosphere to produce gaseous hydrocarbon products (C1-C3). The results with the acidified zeolite, denoted as H-zeolite, are also displayed in the figure. The H-zeolite was found to greatly increase bio-oil yield (34 wt.%) and to double the consumption of hydrogen (0.46 mol $H_2$/kg of glycerol), compared to zeolite. The increase in hydrogen consumption is consistent with the increase in bio-oil yield due to the increase in HDO reactions.

The yield of heavy residue/char for the alumina and zeolite blanks was very small (0.15 and 0.93 wt.% respectively) and not significantly different from the blank (0.23 wt.%). The AC blank exhibited an increased char yield of ~2 wt.%, possibly due to the carbon particles acting as nucleation sites for char formation. The presence of MgO led to a high yield of char (~4.2 wt.%). As mentioned above, the H-zeolite support greatly increased bio-oil oil yield. However, this catalyst also exhibited a dramatic increase in the yield of char (6.0 wt.%). This is likely due to enhanced polymerization/hydro-cracking reactions (evidenced by the increased gas yield) catalyzed by the acidity of the material (Pater et al., 1998; Alonso et al., 2010) and the lack of metals to improve hydrogenation efficiency.

### *3.3.2 Effect of Catalyst Metals*

γ-Alumina was chosen as the reference support material because it is one of the most commonly used catalyst support materials in industry. Ni, Co and Mo were chosen as catalyst metals because they are also commonly used in industry. Alumina-supported Ru catalyst was found to be very effective for conversion of glycerol into hydrogen gas by supercritical water reforming (Byrd et al., 2008). Thus, Ru/$Al_2O_3$ catalyst was also tested in this study. The results using supported metal catalysts are presented in Figure 3-6. As can be seen, the Ni/$Al_2O_3$ catalyst

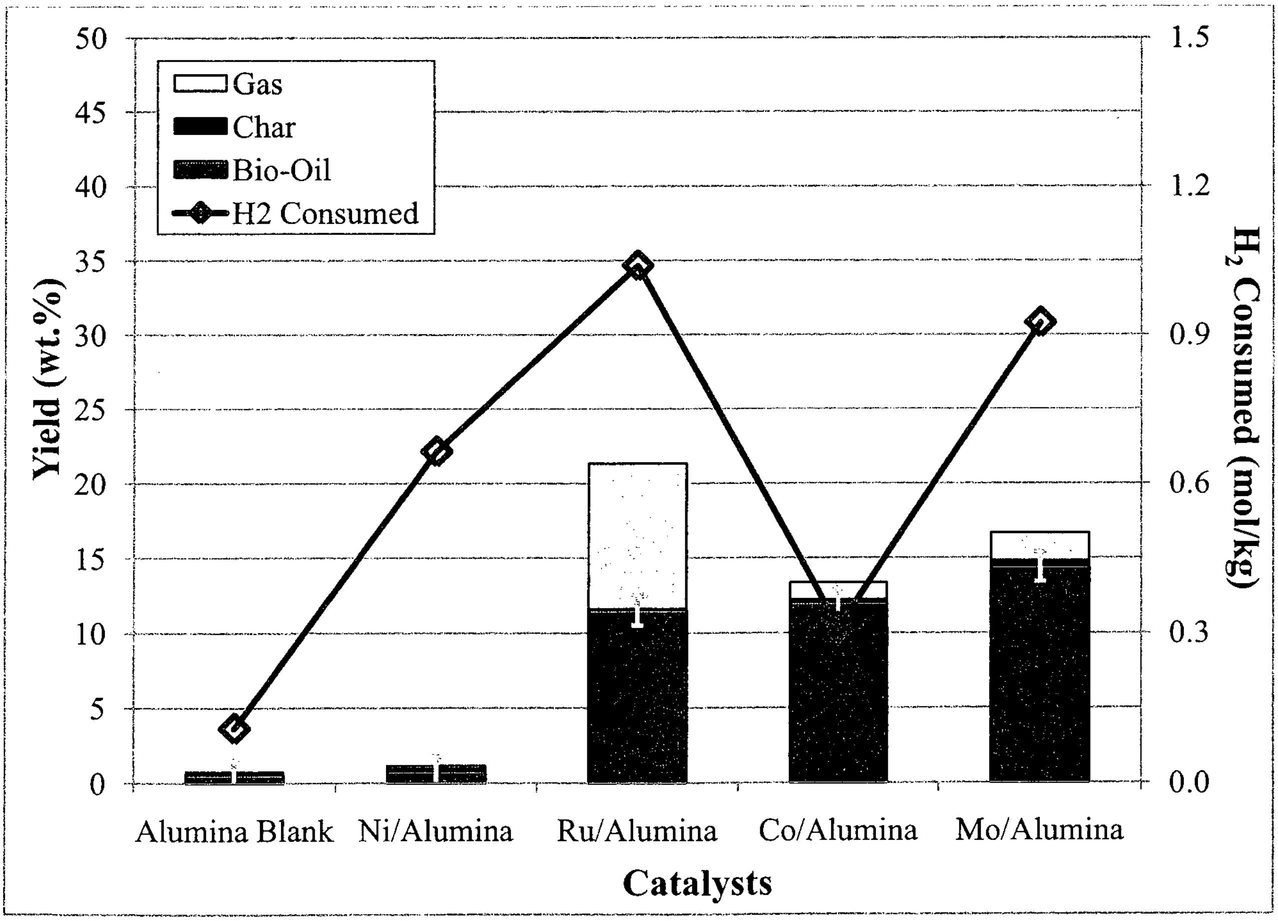


Figure 3-6. Effect of catalyst metals on product yields and $H_2$ consumption (300°C, 60 min).

produced a negligibly small yield of bio-oil of 0.8% - scarcely more than the alumina blank. The $Ru/Al_2O_3$ and $Co/Al_2O_3$ catalysts produced improved bio-oil yields of 11.5 and 12 wt.%, respectively. The gasification of glycerol also increased by metal catalysts, particularly for theRu catalyst reaching 9.7 wt.% of gas. The $Mo/Al_2O_3$ catalyst resulted in the highest bio-oil yield at 14.4 wt.% with a slightly higher level of gasification than the Co catalyst.

The consumption of hydrogen was found to increase in the presence of catalyst metals, even in the case of the Ni which did not produce any bio-oil, possibly indicating that the metals were inducing the reduction and hydro-cracking of glycerol. Hydrogen consumption for the Ni and Mo catalysts reached 0.7 and 0.9 mol/kg. Ru exhibited the highest hydrogen consumption of the catalyst metals tested, accompanied by the highest gas yield. Mo was chosen as the base catalyst for further testing because the Mo catalyst produced the greatest bio-oil yield.

### *3.3.3 Effect of Catalyst Promoters*

A review of available literature reveals that industrial catalysts are rarely prepared with only one catalyst metal loaded onto the support material. In the case of Mo and Co, Mo is often loaded in large proportion as a base metal and Co is added as a promoter to enhance catalytic effectiveness of the Mo. As discussed elsewhere, the addition of P to catalysts is known to enhance HDO reactions and reduce char formation (Yang et al., 2009). The results of these tests are shown in Figure 3-7. The addition of Co promoter to the $Mo/Al_2O_3$ catalyst showed a modest increase of 3.7 wt.% in bio-oil yield, totaling 18.1 wt.%. Glycerol gasification also increased by approximately 50% to 2.7 wt.%. The consumption of hydrogen followed the same positive trend with the addition of various promoters as did the bio-oil yield. This is an expected trend since the deoxygenation and reduction reactions consume hydrogen. The consumption of hydrogen reached a maximum of 2.11 mol/kg with the MoCoP/$Al_2O_3$ catalyst which produced the highest bio-oil yield in this set of experiments at 30.2 wt.% . The increase in bio-oil yield was induced by the addition of only 1.5 wt.% P to the MoCo catalyst. The addition of P also enhanced the gasification of glycerol, more than doubling to 6.1 wt.% and again indicating an improved catalyst activity. Together, these findings confirm the findings of previous research that the addition of P significantly enhances hydrogen addition and oxygen removal activity of the catalyst (Lopez et al. 1990; Lewis et al., 1992; Yang et al., 2009). The addition of Mg to the MoCoP catalyst resulted in a slight decrease in both bio-oil yield and glycerol gasification and slightly lower hydrogen consumption. An interesting result of the MoCoPMg catalyst was that

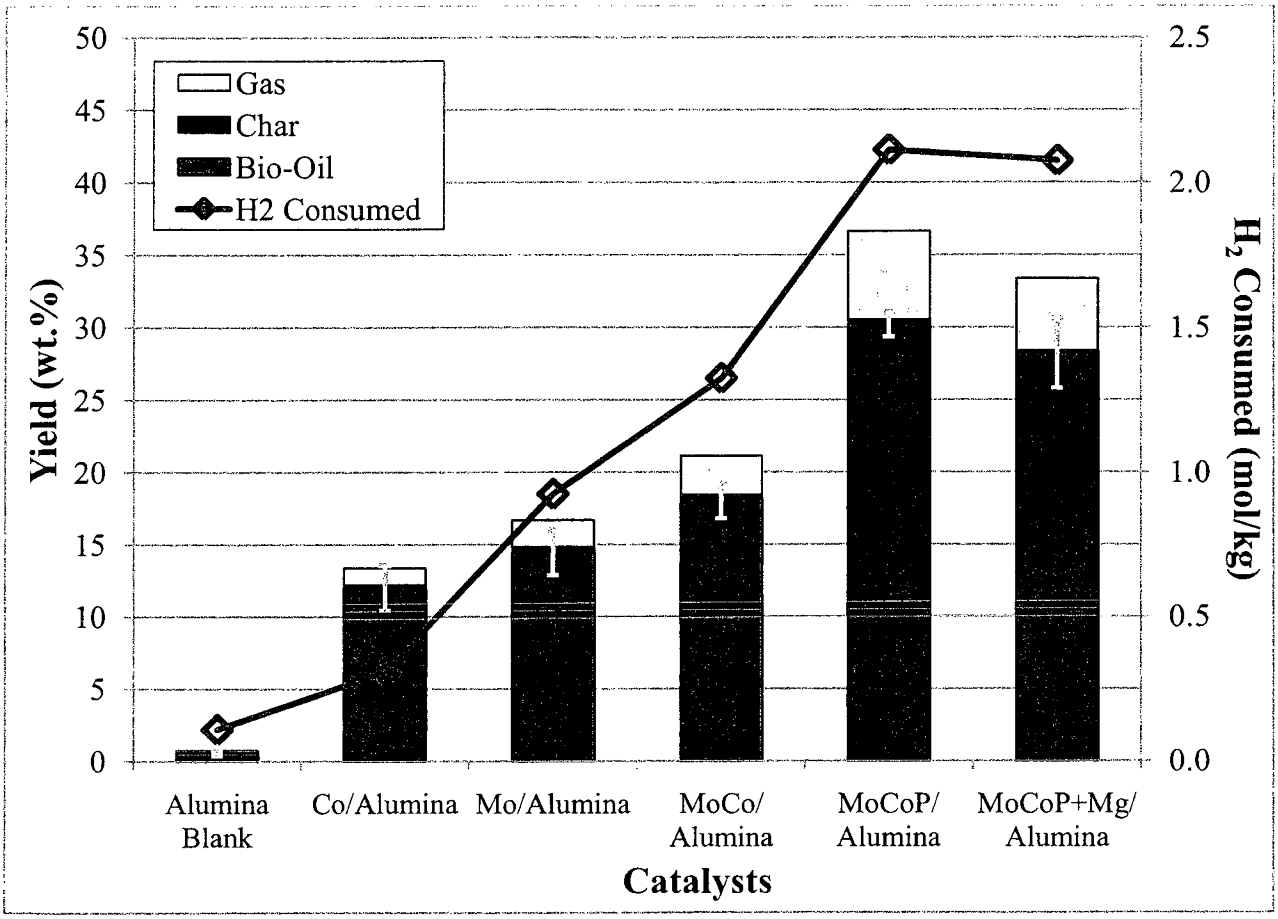


Figure 3-7. Effect of catalyst promoters on product yields and $H_2$ consumption (300°C, 60 min).

almost no char was produced, indicating that the presence of Mg may contribute to reductions in char/solid residue formation over the catalyst. Previous work in the author's laboratory into the HDO of phenol in supercritical hexane demonstrated that CoMoP/MgO was a very active catalyst for HDO (Yang et al., 2009). It has also been observed in previously published research that the addition of phosphorus as a catalyst promoter reduced coke deposition over the HDO catalysts (Czernik et al., 2002; Elliott, 2007).

### *3.3.4 Effect of Catalyst Support on MoCoP Catalyst*

Having determined that MoCoP was the most effective combination of catalyst metals, the effect of support material on metal catalyst activity was investigated. MoCoP catalysts supported on the support media tested earlier were prepared. The results of the tests are presented in Figures 3-8 (a) and (b). Figure 3-8a presents the percentage of the unreacted glycerol found in the aqueous phase (determined by HPLC) after product separation by liquid-liquid extraction. The glycerol conversion (wt%) can then be estimated by 100 wt.% minus the unreacted glycerol (wt%). Comparing the results in Figures 3-8 (a) and (b), generally the conversion of glycerol correlates well with the bio-oil yield for the different catalysts, i.e., a higher glycerol conversion corresponds to a higher bio-oil yield.

The highest glycerol conversion (> 90%) along with the highest bio-oil yield (39.7 wt.%) was obtained with the zeolite-supported MoCoP catalyst, which also consumed the greatest amount of hydrogen (2.3 mol/kg).

Overall, the yield of bio-oil followed the following trend MgO<AC<$Al_2O_3$<zeolite. This trend correlates with the acidity of the support materials indicating that acidity plays an important role in the production of bio-oil. Based on this observed trend, acidified zeolite was

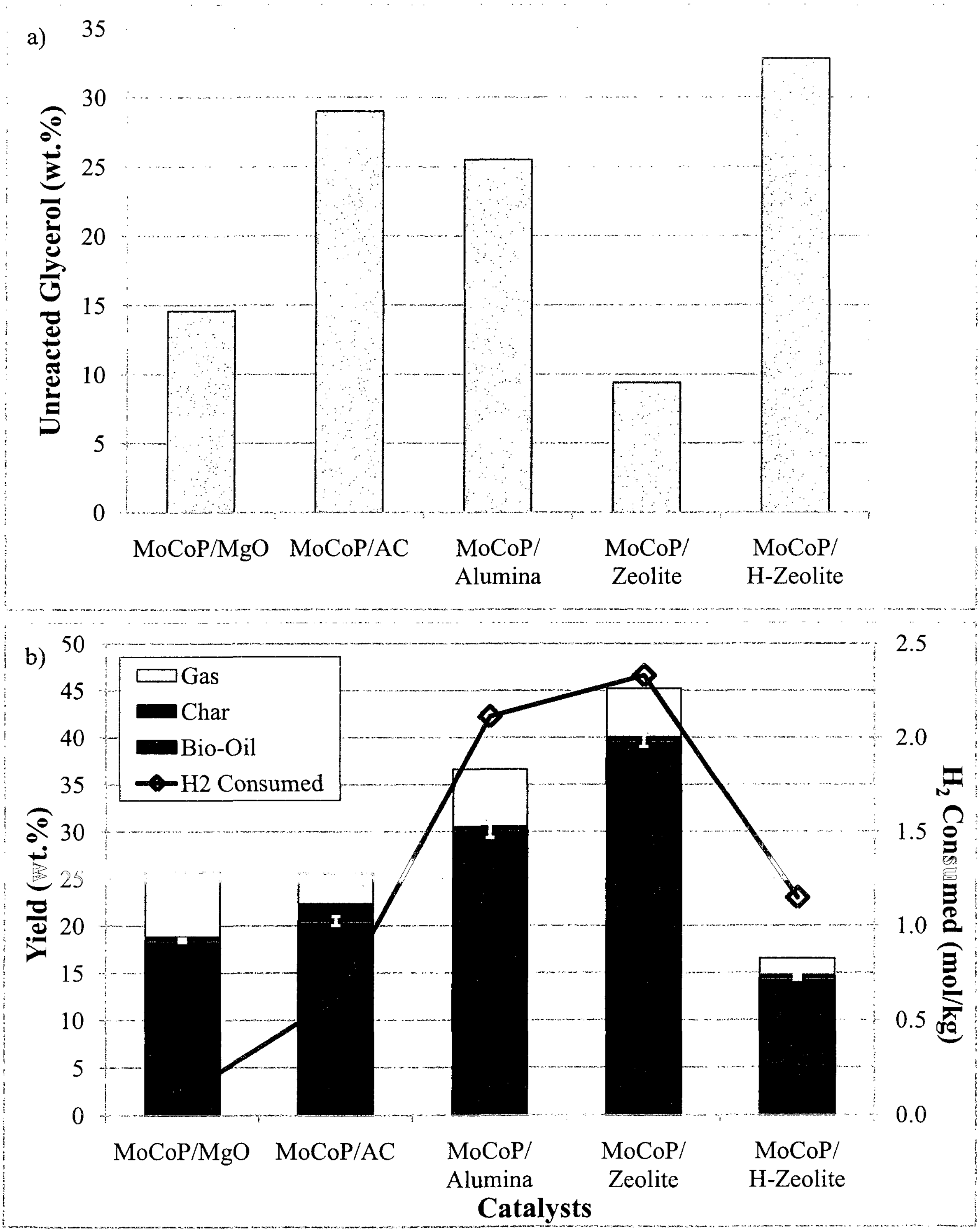


Figure 3-8. Effect of different support materials on glycerol conversion, product yields and $H_2$ consumption with MoCoP catalyst (300°C, 60 min).

prepared by agitating some zeolite in an acidic solution (HCl) then washing, filtering and drying the solids. The acidified zeolite was tested in blank form (as discussed previously) and resulted in a remarkably high bio-oil yield of 34 wt.%. It was expected that the excellent performance of the acidified zeolite would continue or even be enhanced by the addition of catalyst metals. As can be seen in the figure, the activity of the MoCoP/H-zeolite catalyst was found to decrease significantly in terms of bio-oil yield, gasification and hydrogen consumption. The decrease in the catalyst's activity might result from the reduction of its surface area and porosity of the H-zeolite by the addition of catalyst metals. This was evidenced by the $N_2$ isothermal adsorption analyses: the BET surface area and porosity of the MoCoP/H-zeolite were 2.9 $m^2/g$ and 1.44 $\times 10^{-2}$ cc/g, compared with 67.3 $m^2/g$ and $4.96\times 10^{-2}$ cc/g for the H-zeolite. The deactivation of the MoCoP/H-zeolite catalyst might also be due to the formation of less active metal chloride species, i.e., $\beta$-$MoCl_2$ as detected by XRD (Figure 3-2).

### *3.3.5 Effect of Catalyst Metal Chemistry*

The chemical state of the catalyst metals was investigated and found to significantly affect the conversion of glycerol and the yield of bio-oil as seen in Figures 3-9a and 3-9b, respectively. Samples of the $Al_2O_3$- and zeolite-supported MoCoP catalysts from the previous experiments were reduced in a flow reactor under a hydrogen atmosphere at 450°C for 4 h. The reduction of MoCoP catalysts was found to significantly decrease conversion of glycerol and the yield of bio-oil. For instance, reduction of both zeolite-supported MoCoP catalyst decreased conversion of glycerol from 90% to 60%, and the yield of bio-oil from ~38.5 wt.% to ~5 wt.%. Hydrogen consumption and glycerol gasification decreased as well. The decrease in glycerol gasification and hydrogen consumption can be related to the decrease in bio-oil yield according to the

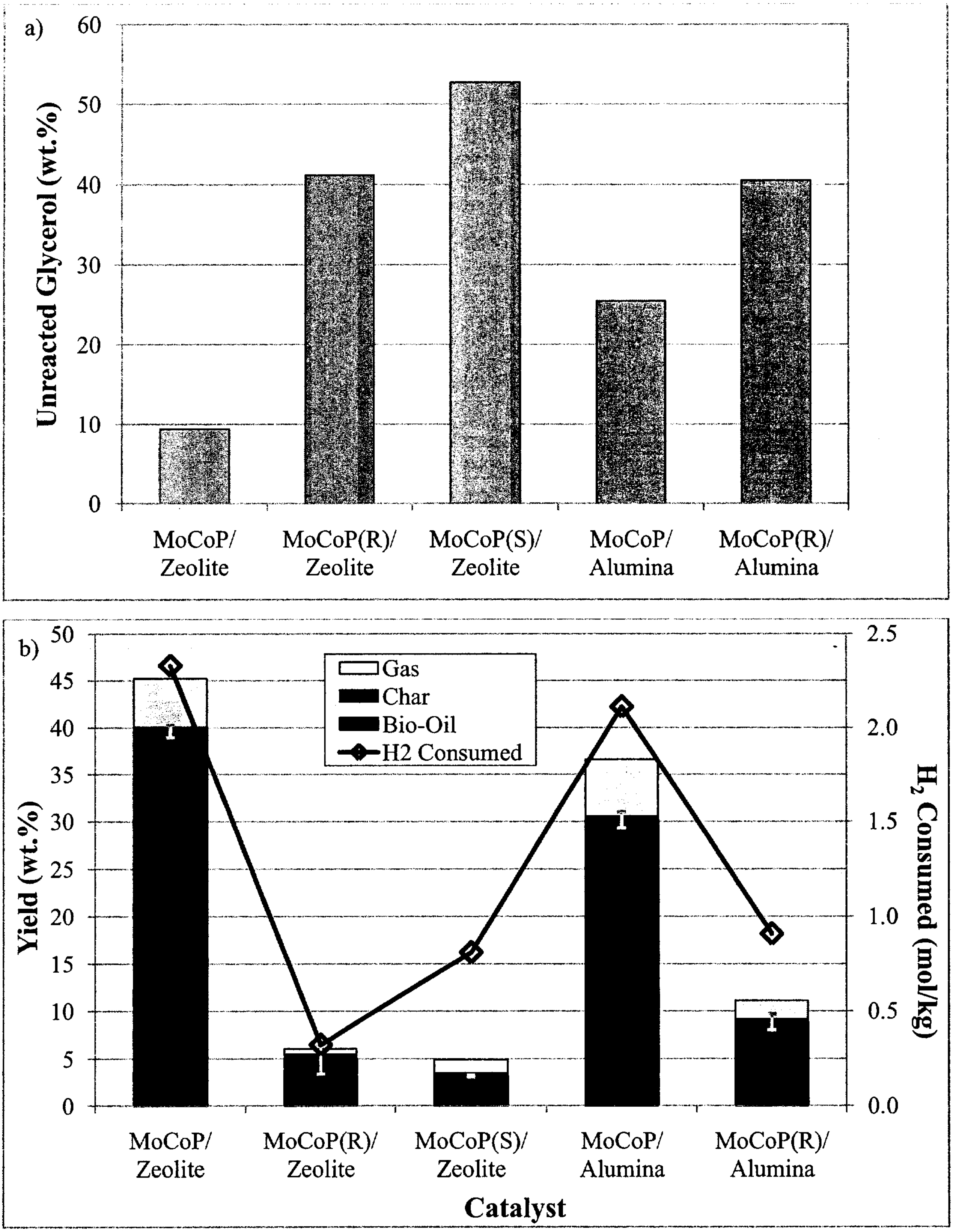


Figure 3-9. Effect of catalyst metal chemistry on glycerol conversion, product yields and $H_2$ consumption (300°C, 60 min).

rationale as was discussed in the previous sections. It is also possible that the increased hydrogen consumption of the oxidized catalysts may, in part, be due to reduction of oxidized metal sites *in situ* during the HDO reaction. The large decrease in the effectiveness of the reduced catalysts in terms of bio-oil yield and hydrogen consumption, as compared to the catalysts in their oxidized forms, suggests that catalyst metal oxides play a critical role in HDO reactions and the formation of bio-oil. More research is needed to elucidate the specific reaction mechanisms responsible.

The zeolite-supported catalyst was also tested in its sulfided form. Interestingly, the sulfided catalyst was found to decrease bio-oil yield to an even greater extent than the reduced catalyst. This is contrary to the results published in many studies on the HDO of bio-oil where sulfided catalysts (NiMo or CoMo) were commonly used (Centeno et al., 1995; Klipcera and Zrdazil, 2002; Zdražil, 2003; Yang et al., 2009). Based on this finding, sulfidation of the $Al_2O_3$-supported MoCoP catalyst was not performed. The decreased activity of the sulfided catalyst may be caused in part by a decrease in pore size (3.4 nm as compared to 10.1 nm for MoCoP/zeolite) due to the deposition of S on the catalyst, as evidenced by the results of the porosity analyses on the catalysts. However, hydrogen consumption for the sulfided catalyst increased as compared to the reduced catalyst. This increase can be explained by reduction of the sulfided metals in the catalyst during the reaction and consequent production of $H_2S$. The formation of $H_2S$ was unable to be verified in this work due to the GC-TCDs being incapable of detecting $H_2S$.

### *3.3.6 Product Characterization*

Carbon balances were calculated for a number of catalysts in this study in order to evaluate the material balance of the HDO operations. The carbon compositions of the HDO products (bio-oils and the aqueous products) were analyzed with an elemental analyzer and DOC. The carbon content of the spent catalyst was determined indirectly by TGA, and the carbon content of the gaseous products was obtained by GC-TCD. Carbon recovery in the products was defined by the percentage of the moles of carbon in the products in relation to the moles of carbon originally present in the glycerol prior to hydrodeoxygenation. Some typical results of the carbon balance, calculated by summing the carbon recovery for all of the products, are presented in Table 3-3. As indicated in Table 3-2, the overall carbon molar conservation fell in a reasonable range of 91.5-106% in most operations, except for the operations with MoCoP/zeolite (reduced) and MoCoP/H-zeolite catalysts, suggesting generally acceptable mass conservation and reliable experimental data. The carbon balances for the catalysts that performed poorly in terms of bio-oil yield generally exhibited a greater deviation from unity than did the carbon balances for the better-performing catalysts. It is believed that the discrepancies could be attributed to variability in the DOC results performed on the aqueous products. The samples supplied to the laboratory for analysis were too concentrated for the instrument and had to be diluted 4,000 times to obtain useable concentrations. TGA analysis was not performed on the AC-supported catalyst or the sulfided MoCoP catalysts since relevant data would not have been produced. The greater-than-

Table 3-3. Carbon recovery in the products of the hydrodeoxygenation of glycerol with and without catalyst (300°C, 5.0 MPa $H_2$, 60 min)

| **Catalyst** | **Carbon Recovery in Products (%)** | | | | **Carbon Balance (%)** |
|---|---|---|---|---|---|
| | **Bio-Oil** | **Aqueous** | **Char** | **Gas** | |
| MoCoP/MgO | 32.4 | 60.5 | 1.0 | 5.8 | 99.8 |
| MoCoP/AC | 36.7 | 66.4 | n/r | 2.8 | 106.0 |
| MoCoP/$Al_2O_3$ | 52.3 | 35.6 | 0.9 | 14.7 | 103.5 |
| MoCoP/Zeolite | 75.7 | 11.8 | 1.1 | 11.4 | 100.0 |
| MoCoP/zeolite (reduced) | 10.3 | 65.4 | 1.3 | 1.7 | 78.7 |
| MoCoP/zeolite (sulfided) | 5.2 | 80.3 | n/r | 6.1 | 91.5 |
| MoCoP/H-zeolite | 23.4 | 53.4 | 1.2 | 4.1 | 82.1 |
| H-zeolite | 25.7 | 56.4 | 16.3 | 2.9 | 101.4 |

unity carbon balance for the AC-supported catalyst may be due to the incorporation of carbon from the support material into the liquid and gaseous products.

The properties of the bio-oil products are of a particular interest in this work. The viscosities of all of the bio-oils were found to be much higher than straight chain alkanes and fell in the range of 158-786 cP. The elemental compositions (C, H and N) of some typical bio-oil products are presented in Table 3-4, where the elemental composition of the glycerol feedstock is also given for comparison. The oxygen contents of the samples were obtained by difference assuming negligible sulfur content, and the higher heating value (HHV) of each sample was calculated by the Dulong formula, i.e., HHV (MJ/kg) = $0.3383C + 1.422 (H - O/8)$ where C, H and O were obtained from the elemental analysis. Compared with the glycerol feedstock, all of the bio-oil samples exhibited much higher carbon contents and lower concentrations of oxygen leading to significantly increased higher heating values. All of the bio-oils produced exhibited HHV values around 30 MJ/kg as compared to only 16 MJ/kg for the glycerol. Accordingly, with the maximum bio-oil yield of about 40 wt.% obtained from hydrodeoxygenation in the presence of MoCoP/zeolite catalyst as shown in Figure 3-8, about 75% of the energy in the feedstock was recovered in the bio-oil product. This result suggests that hydrodeoxygenation of glycerol in the presence of suitable catalysts can be a promising technique (due to the relatively mild temperature conditions) for upgrading low-heating value glycerol to a liquid bio-crude with a significantly increased heating value. As also shown in the table, all of the bio-oil samples have very similar O/C ratios (0.18 ~ 0.34, avg. 0.26) and H/C ratios (1.18 ~ 1.41, avg. 1.32), both of which are much lower than those of the glycerol feedstock (1.0 and 2.67 respectively), which suggests that high concentrations of condensed aromatic compounds are present in the bio-oil products, as evidenced by the GC/MS results to be discussed later.

Table 3-4. Elemental compositions of bio-oils obtained from different catalysts (300°C, 5MPa $H_2$, 60 min).

| Bio-Oil | Elemental Composition (wt.%) | | | | | HHV (2) | Empirical Formula | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | S | O (1) | (MJ/kg) | C | H | O | S |
| Glycerol | 39.1 | 8.8 | 0.0 | - | 52.1 | 16 | 1 | 2.67 | 1 | - |
| MoCo/MgO | 72.0 | 8.5 | 0.0 | - | 19.6 | 33 | 1 | 1.40 | 0.20 | - |
| MoCo/$Al_2O_3$ | 69.1 | 7.5 | 0.0 | - | 23.5 | 30 | 1 | 1.29 | 0.26 | - |
| MoCoP/MgO | 69.1 | 8.1 | 0.0 | - | 22.8 | 31 | 1 | 1.40 | 0.25 | - |
| MoCoP/MgO+zeolite | 70.2 | 8.2 | 0.0 | - | 21.6 | 32 | 1 | 1.39 | 0.23 | - |
| MoCoP/AC | 69.0 | 7.6 | 0.0 | - | 23.4 | 30 | 1 | 1.31 | 0.25 | - |
| MoCoP/$Al_2O_3$ | 69.1 | 7.3 | 0.0 | - | 23.6 | 30 | 1 | 1.26 | 0.26 | - |
| MoCoP/$Al_2O_3$ (red.) | 68.5 | 7.8 | 0.0 | - | 23.7 | 30 | 1 | 1.36 | 0.26 | - |
| MoCoP+Mg/$Al_2O_3$ | 70.8 | 7.8 | 0.0 | - | 21.4 | 31 | 1 | 1.31 | 0.23 | - |
| MoCoP/zeolite | 74.0 | 7.5 | 0.0 | - | 18.5 | 32 | 1 | 1.20 | 0.19 | - |
| MoCoP/zeolite (red.) | 65.9 | 6.6 | 0.0 | - | 27.5 | 27 | 1 | 1.18 | 0.31 | - |
| MoCoP/zeolite (sulf.) | 64.9 | 7.7 | 0.0 | 0.5 | 27.0 | 28 | 1 | 1.41 | 0.31 | 0.0 |
| MoCoP/H-zeolite | 63.8 | 7.3 | 0.0 | - | 28.9 | 27 | 1 | 1.36 | 0.34 | - |
| zeolite blank | 65.6 | 8.1 | 0.0 | - | 26.4 | 29 | 1 | 1.47 | 0.30 | - |
| H-zeolite | 69.0 | 6.8 | 0.0 | - | 24.2 | 29 | 1 | 1.18 | 0.26 | - |

[1] By difference and assuming that the sulfur content is negligible;

[2] Higher heating value (HHV) calculated by the Dulong Formula, i.e., HHV (MJ/kg) = 0.3383C + 1.422 (H – O/8)

The GC/MS chromatograms of bio-oils from the HDO of glycerol with MoCoP/zeolite and MoCoP/$Al_2O_3$ catalysts are presented in Figure 3-10, in comparison with those of the blank test and the original glycerol. An abridged table comparing some of the compounds in Figure 3-10 is provided in Table 3-5. The table lists the area % for some of the compounds (defined by percentage of the compound's chromatographic area out of the total area) and the total area % for those compounds that are listed. It is interesting to note that seen from the table, the bio-oils from the catalytic runs consist of a high proportion of phenol derivatives and ketones, e.g., 2-methyl phenol and hexanone. Also, in the case of the bio-oil blank, there is a large fraction of unreacted glycerol present. This peak is visible to a lesser extent in the bio-oil from the $Al_2O_3$-supported catalyst and is virtually non-existent for the zeolite-based bio-oil. These results are consistent with the trend observed in the catalytic activities of these catalysts for the glycerol conversion

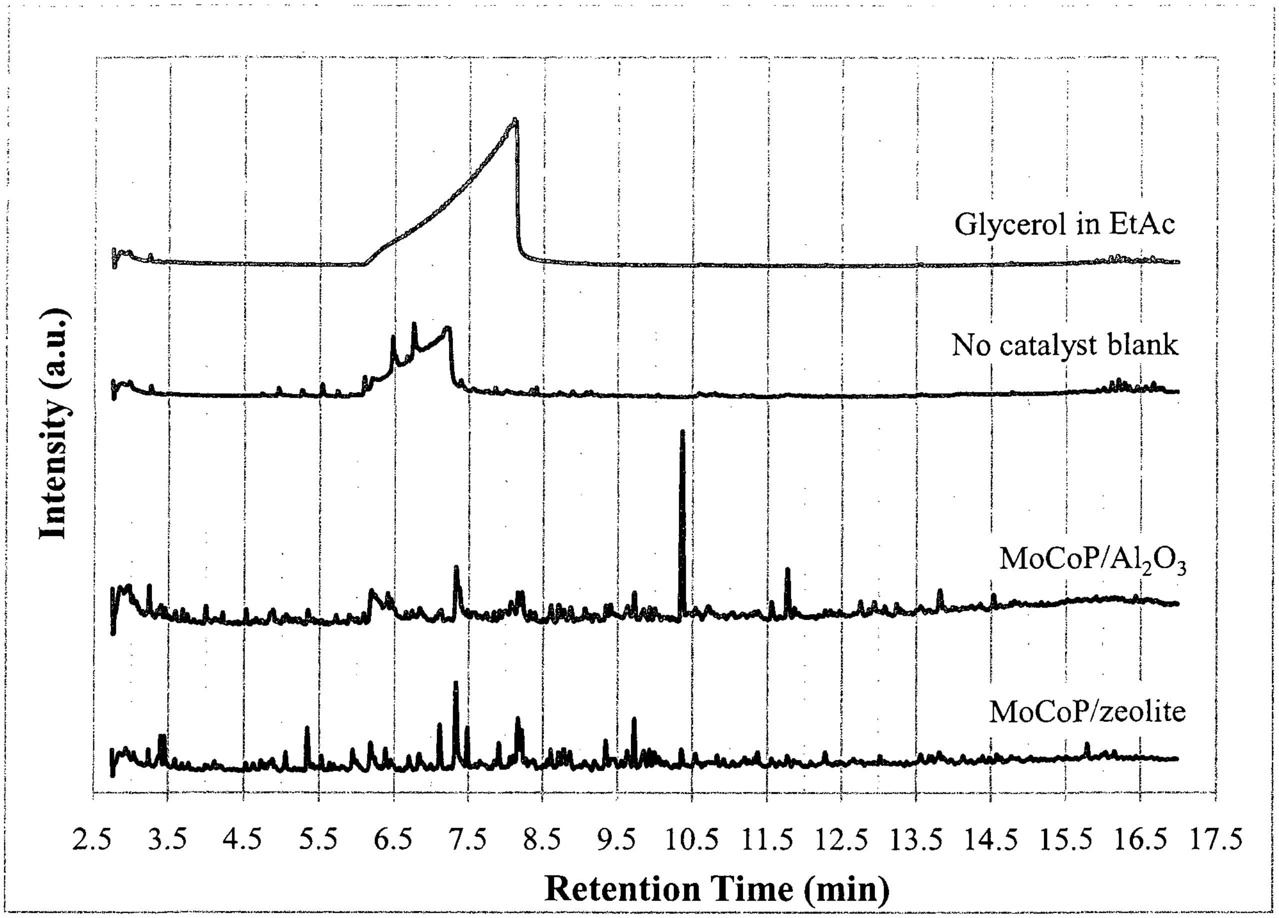


Figure 3-10. GC/MS chromatograms of bio-oils from the HDO of glycerol with and without MoCoP catalysts

Table 3-5. Comparison of the GC/MS results for various bio-oils from HDO of glycerol (300°C, 5.0 MPa $H_2$, 60 min).

| **Peak** | **RT** | **Compound** | **Area (%)** | | | |
|---|---|---|---|---|---|---|
| | | | **MoCoP /zeolite** | **MoCoP /$Al_2O_3$** | **No Catalyst** | **Glycerol in EtAc** |
| 1 | 3.4 | 3-HEXANONE | 2.45 | 1.91 | | |
| 2 | 3.45 | 2-HEXANONE | 1.74 | 0.76 | | |
| 3 | 5.336 | 2,5-HEXANEDIONE | 3.02 | 0.92 | | |
| 4 | 6.185 | PHENOL | 2.65 | 2.65 | 4.49 | |
| 5 | 6.384 | 3,4-DIMETHYL-2-CYCLOPENTEN-1-ONE | 2.18 | | | |
| 6 | 6.474 | 2-ETHYL-1,3-DIOXOLANE-4-METHANOL | | | 23.73 | |
| 7 | 6.669 | 1,2,3-PROPANETRIOL | | 3.62 | 51.94 | 100 |
| 8 | 7.112 | 2,3-DIMETHYL-2-CYCLOPENTEN-1-ONE | 3.86 | | | |
| 9 | 7.328 | 2-METHYL PHENOL | 9.36 | 6.62 | | |
| 10 | 7.388 | 2-(1,1-DIMETHYLETHOXY) ETHANOL | | | 2.27 | |

Table 3-5.Continued

| **Peak** | **RT** | **Compound** | **Area (%)** | | | |
|---|---|---|---|---|---|---|
| | | | **MoCoP /zeolite** | **MoCoP /$Al_2O_3$** | **No Catalyst** | **Glycerol in EtAc** |
| 11 | 7.481 | 2,3,4-TRIMETHYL-2-CYCLOPENTEN-1-ONE | 2.94 | | | |
| 12 | 7.652 | 4-METHYL PHENOL | 2.04 | | | |
| 13 | 7.91 | 2-CYCLOPENTEN-1-ONE, 2,3,4-TRIMETHYL- | 2.1 | | | |
| 14 | 8.162 | 2,6-DIMETHYL PHENOL | 4.14 | 1.86 | | |
| 15 | 8.217 | 2-METHYL BENZOFURAN | 3.05 | 1.98 | | |
| 16 | 8.785 | 2,4-DIMETHYL PHENOL | 2.29 | | | |
| 17 | 9.343 | 2-ETHYL-5-METHYL PHENOL | 2.41 | | | |
| 18 | 9.723 | 4,7-DIMETHYLBENZOFURAN | 3.22 | 1.31 | | |
| 19 | 9.855 | 4-PROPYL PHENOL | 2.36 | | | |
| 20 | 10.36 | 1-(2-HYDROXY-5-METHYLPHENYL) ETHANONE | | 8.93 | | |
| 21 | 11.76 | 1,2-(METHYLENEDIOXY)-4-PROPYL BENZENE | | 2.74 | | |
| **Total** | | | **49.81** | **33.3** | **80.16** | **100** |

and the bio-oil yields (i.e., zeolite>$Al_2O_3$>blank). A more complete analysis of the bio-oil from oxidized MoCoP/zeolite catalyst is provided in Table 3-6.

As can be seen in this table, and was mentioned above, the majority of the compounds in the bio-oil are aromatics (37% of the total) and ketones (41% of the total) mostly in the C6-C9range. These findings confirm the H/C and O/C ratios (average 1.32 and 0.20 respectively) obtained from the CHN analysis presented previously in Table 3-3. The aromatics are mostly present in the form of substituted phenols condensed from the fragments of partially deoxygenated glycerol. The presence of ketone and quinone structures indicates that the deoxygenation of glycerol under present conditions was not complete and that more effective HDO catalysts or conditions are needed to obtain bio-crude oils with lower oxygen contents.

Table 3-6. GC/MS analysis of the bio-oil from HDO of glycerol with MoCoP/zeolite catalyst

| RT (min) | Area% | Compound |
|---|---|---|
| 2.932 | 2.18 | *4-METHYL-2-PENTANONE* |
| 3.042 | 1.29 | 1-PROPOXY BUTANE |
| 3.233 | 0.69 | **TOLUENE** |
| 3.4 | 2.45 | *3-HEXANONE* |
| 3.45 | 1.74 | *2-HEXANONE* |
| 4.878 | 1.53 | *4-METHYLCYCLOHEXANONE* |
| 5.051 | 1.26 | *2-METHYL-2-CYCLOPENTEN-1-ONE* |
| 5.336 | 3.02 | *2,5-HEXANEDIONE* |
| 5.527 | 1.49 | *2,3-DIMETHYL-2-CYCLOPENTEN-1-ONE,* |
| 5.948 | 1.79 | *3-METHYL-2-CYCLOPENTEN-1-ONE* |
| 6 | 1.27 | *2,2,5-TRIMETHYL-3,4-HEXANEDIONE* |
| 6.185 | 2.65 | **PHENOL** |
| 6.233 | 1.33 | 5-METHYL-2-(1-METHYLETHYL)-CYCLOHEXANOL |
| 6.384 | 2.18 | *3,4-DIMETHYL-2-CYCLOPENTEN-1-ONE* |
| 6.698 | 1.26 | 1,4-DIONE-2-METHYL-2,5-CYCLOHEXADIENE |
| 6.838 | 1.59 | *5-ETHYLDIHYDRO-5-METHYL-2(3H)-FURANONE* |
| 7.112 | 3.86 | *2,3-DIMETHYL-2-CYCLOPENTEN-1-ONE* |
| 7.328 | 9.36 | **2-METHYL PHENOL** |
| 7.481 | 6.28 | *2,3,4-TRIMETHYL-2-CYCLOPENTEN-1-ONE* |
| 7.652 | 2.04 | **4-METHYL PHENOL** |
| 7.852 | 1.17 | 6,6-DIMETHYL-2-METHYLENEBICYCLO(3.2.0)HEPTAN-3-OL |
| 8.061 | 1.7 | *3,5-OCTADIEN-2-ONE* |
| 8.165 | 4.14 | **2,6-DIMETHY PHENOL** |
| 8.217 | 3.05 | **2-METHYL BENZOFURAN** |
| 8.275 | 0.94 | *2,6-DIMETHYL-2,5-CYCLOHEXADIENE-1,4-DIONE* |
| 8.376 | 2.02 | *2,3,4,5-TETRAMETHYL-2-CYCLOPENTEN-1-ONE* |
| 8.508 | 1.01 | *4-ISOPROPYLCYCLOHEX-2-EN-1-ONE* |
| 8.608 | 1.59 | **2-ETHYL PHENOL** |
| 8.714 | 1.64 | 2-PROPENYL-TRANS-2-METHYL-2-BUTENOATE |
| 8.785 | 2.29 | **2,4-DIMETHYL PHENOL** |
| 8.866 | 2.14 | *2-CYCLOPENTYL-1-(1H-IMIDAZOL-4-YL)-ETHANONE* |
| 9.197 | 1.11 | 2,4-DIMETHYL-3-CYCLOHEXENE-1-CARBALDEHYDE |
| 9.343 | 2.41 | **2-ETHYL-5-METHYL PHENOL** |
| 9.723 | 3.22 | **4,7-DIMETHYL BENZOFURAN** |
| 9.855 | 2.36 | **4-PROPYL PHENOL** |
| 9.932 | 1.47 | *3-METHYL-2-(1-METHYLETHYL) CIS-CYCLOHEXANONE* |
| 9.996 | 1.39 | **2-METHYL-2-INDANOL** |
| 10.054 | 0.96 | **2,4,5-OR 2,3,5-TRIMETHYL PHENOL** |
| 10.155 | 1.16 | *3,4,5,6-TETRAMETHYL-2H-PYRAN-2-ONE* |
| 10.359 | 1.2 | *1-(2-HYDROXY-5-METHYLPHENYL)-ETHANONE* |

Table 3-6. continued

| RT (min) | Area% | Compound |
|---|---|---|
| 11.762 | 1 | **1,2-(METHYLENEDIOXY)-4-PROPYL BENZENE** |
| 11.85 | 0.96 | **2-ETHYL-5-PROPYL PHENOL** |
|  | 88.19 | Total area |
|  | **37.11** | **Total aromatics** |
|  | *40.55* | *Total ketones* |
|  | 10.53 | Remaining compounds |

A comparison of the GC/MS results for the bio-oils from the HDO of glycerol with H-zeolite, MoCoP/H-zeolite and MoCoP/zeolite catalysts are presented in Figure 3-11. It is interesting to note that the bio-oil from the H-zeolite blank, even though the bio-oil yield was very high (34%), contains fewer aromatic compounds than the MoCoP/zeolite bio-oil. The fraction of ketones is also lower. Instead, the bulk of the oil consists of high concentrations of alcohols and ethers.

The differences between the oxidized, reduced and sulfided forms of the MoCoP/zeolite catalyst are evident not only in their activities for bio-oil yields but also in the composition of the bio-oils. GC/MS chromatograms of these oils are presented in Figure 3-12. The most obvious difference in bio-oil composition between the three catalysts is the presence of unreacted glycerol in the reduced and sulfided bio-oils, as evidenced by the poor glycerol conversion and bio-oil yields for the two catalysts in question (Figure 3-9). In addition, although the bio-oils from both the reduced and sulfided catalysts contain aromatics, they are not as abundant as in the bio-oil from the oxidized catalyst. The oil from the sulfided catalyst contains more alcohols than the other two bio-oils. This suggests that the sulfided catalyst is not as effective in deoxygenating the glycerol as the reduced and especially the oxidized forms are. Also of note is that some sulfur compounds were identified in the bio-oil from the sulfided catalyst, e.g., 1-(3-thienyl)-ethanone

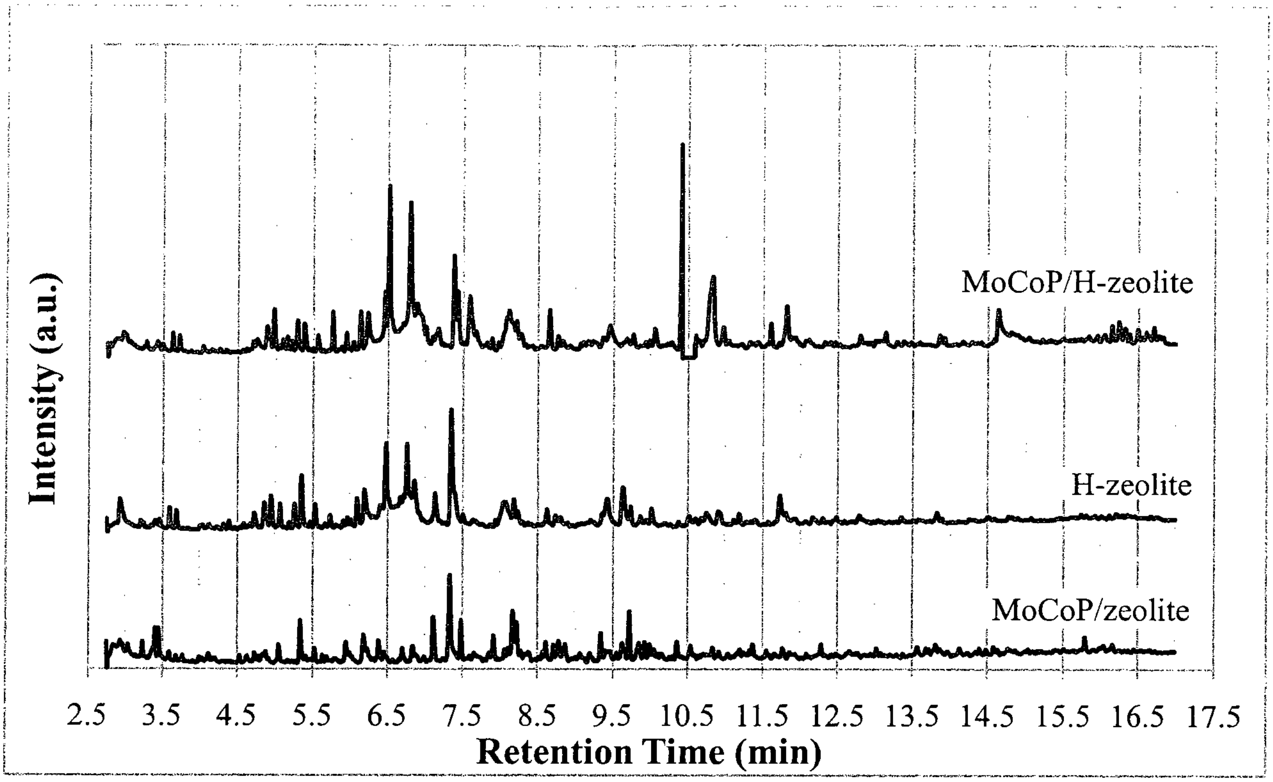


Figure 3-11. GC/MS chromatograms of bio-oils from the HDO of glycerol with H-zeolite, MoCoP/H-zeolite and MoCoP/zeolite catalysts

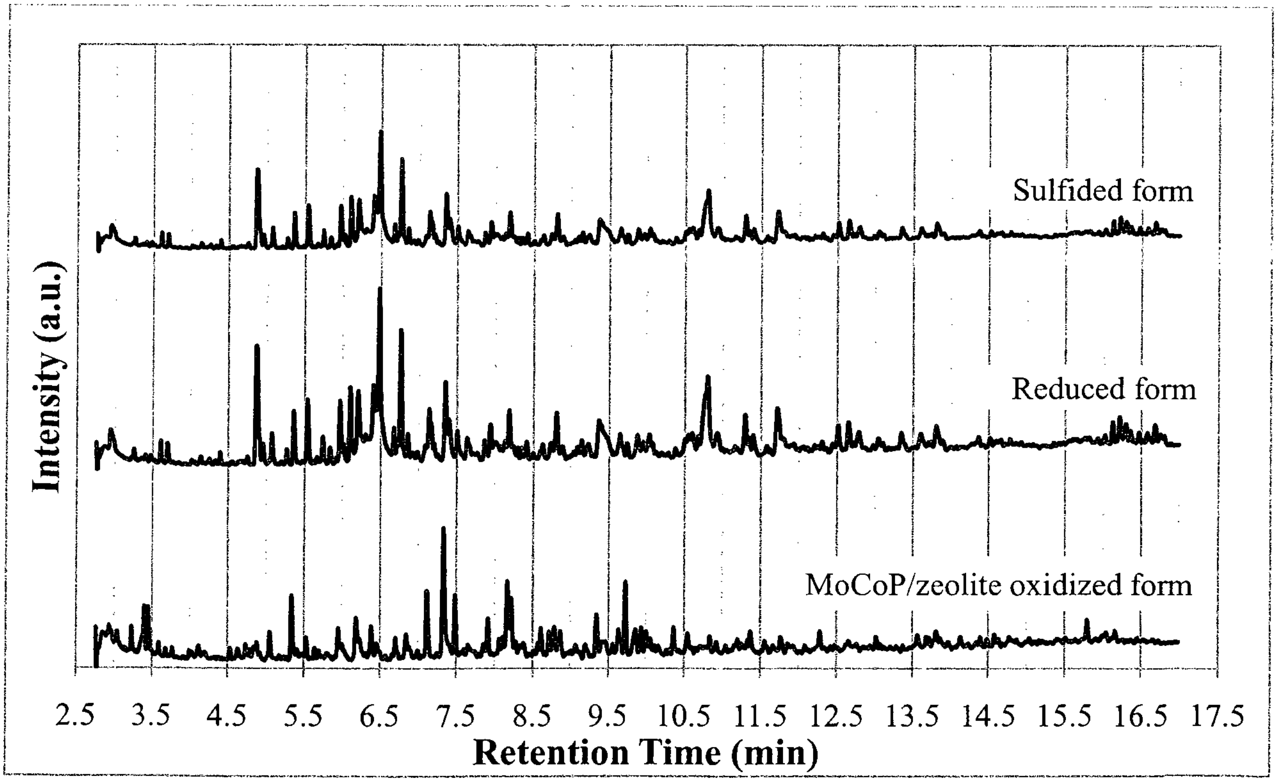


Figure 3-12. GC/MS chromatograms of bio-oils from the HDO of glycerol with the oxidized, reduced and sulfided forms of MoCoP/zeolite catalyst

and benzothiazole. The presence of sulfur compounds was consistent with the CNS analysis of the oil which indicated that sulfur comprised 0.48 wt.% of the bio-oil.

Simulated distillation was performed on bio-oils from the MoCoP/zeolite catalyst and the acidified zeolite blank to confirm the GC/MS results. These oils were chosen on the basis of the performance of the MoCoP/zeolite and the unexpectedly high yield for the H-zeolite blank. The simulated distillation was calibrated using C5 to C60 standards. As seen in Figure 3-13, the majority (~95%) of the components in the bio-oils have boiling points less than 165°C indicating that the components are lighter and more volatile than is typically found with heavy oils. This is consistent with the previous findings that the majority of the bio-oil components were in the C6 to C9 range.

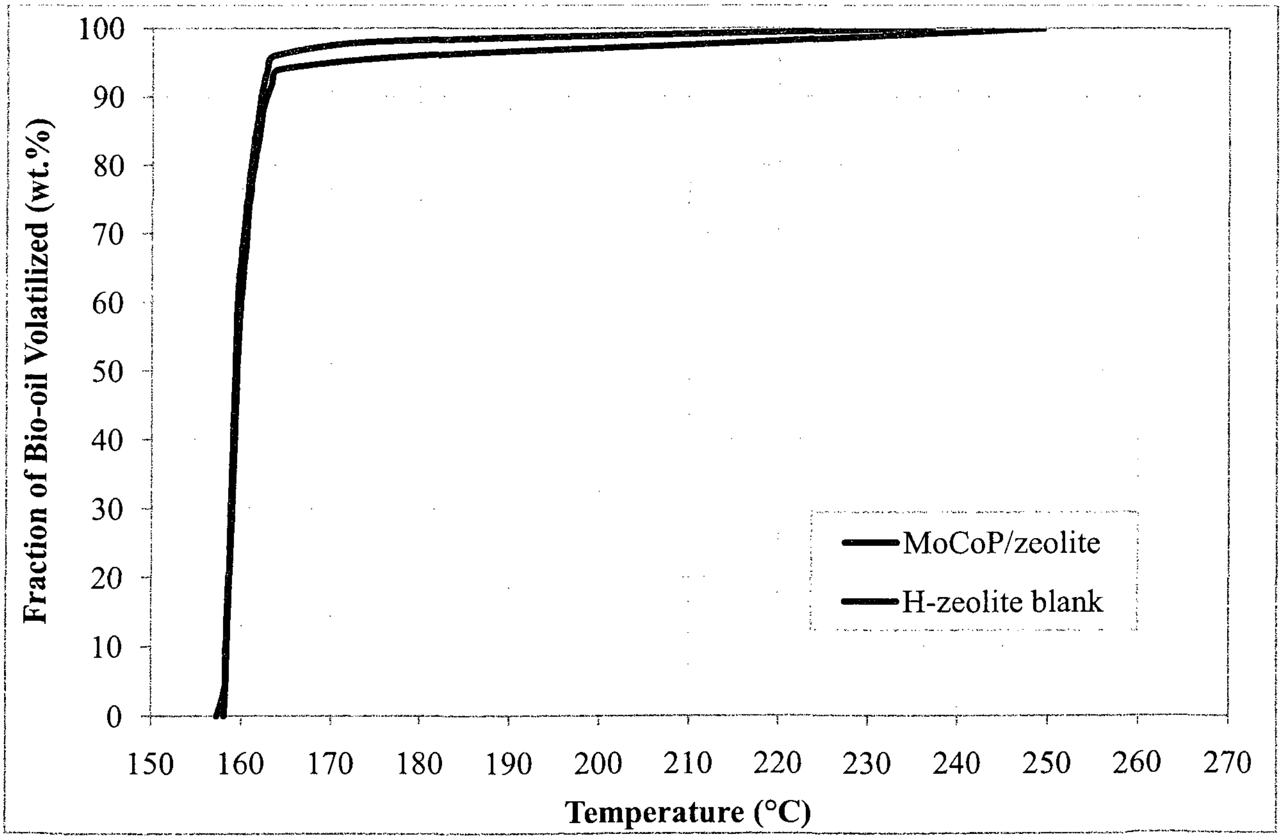


Figure 3-13. Simulated distillation of MoCoP/zeolite and H-zeolite bio-oils

### *3.3.7 Characterization of Spent Catalysts*

As discussed previously (Figure 3-1), the fresh (as-synthesized) catalysts were characterized by powder X-ray diffraction (XRD) using Cu-Kα radiation after calcination, reduction and sulfidation. Samples of these same catalysts were analyzed after reaction in order to investigate the changes in the crystalline structures of the catalysts during the reaction. The resulting XRD patterns are presented in Figure 3-14. Compared with those in the fresh oxidized MoCoP catalyst supported either on $Al_2O_3$ or zeolite, the $MoO_3$ signals in the spent catalysts significantly weaken or become undetectable probably due to the masking effects of the deposited coke or solid residue from glycerol.

In the spent oxidized MoCoP/zeolite catalyst, the zeolite signals are nearly undetectable, which may be attributed to the presence of carbon, in the form of heavy residue and char,

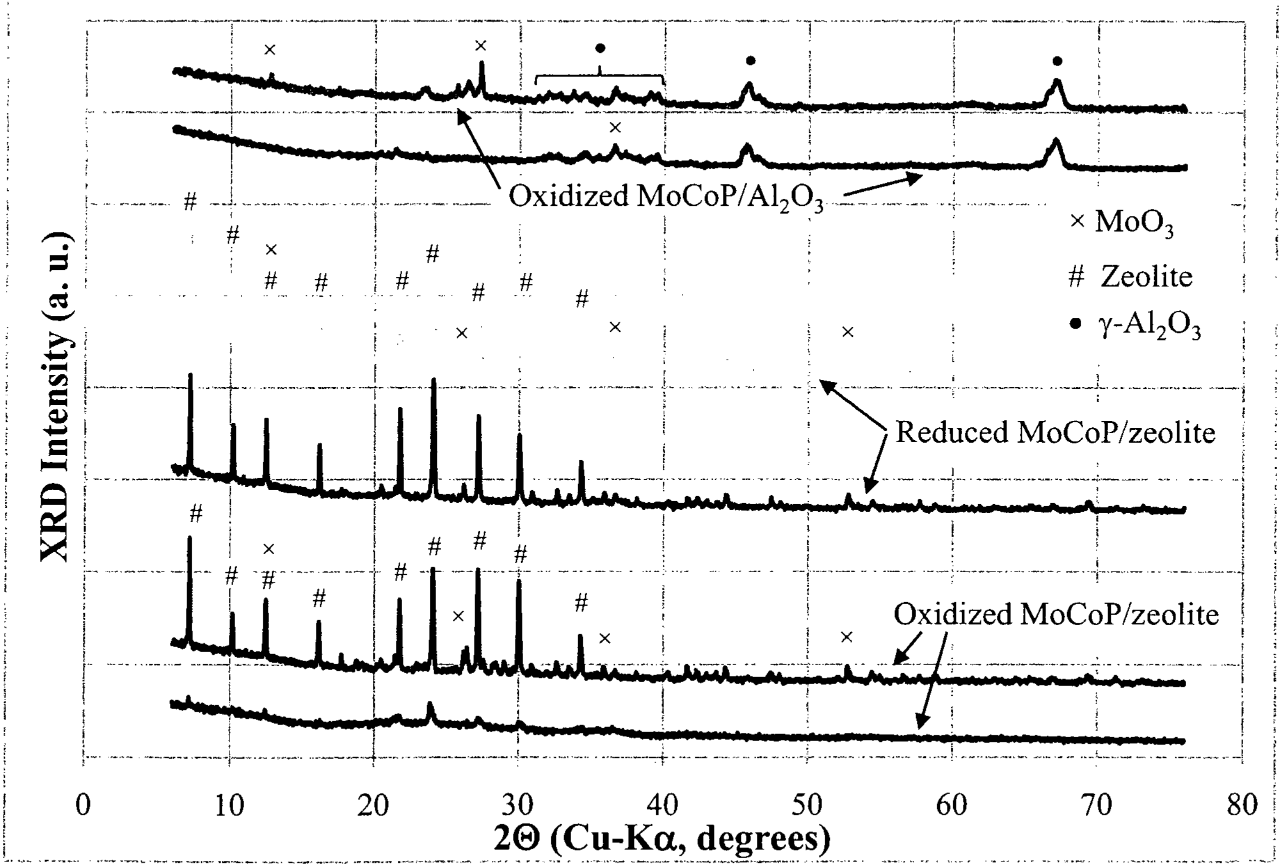


Figure 3-14. XRD patterns of the fresh (upper) and spent (lower) catalysts

masking the support material from the X-rays. This effect was not noticed with the reduced and sulfided catalysts due to their poorer HDO activity and, consequently, much lower deposition of carbonaceous material. Although it is difficult to see at the scale of the figure, there is a broad shoulder centered around $2\Theta = 24°$ for the spent oxidized MoCoP/zeolite catalyst which is indicative of the presence of amorphous carbon.

Thermal gravimetric analysis (TGA) was performed on the all of the spent catalysts, except the sulfided and AC-supported catalysts, in order to determine the amount of char and heavy residue present. The TGA profiles were collected using the spent catalysts heated at 30 K/min from room temperature up to 900°C in 40 ml/min flow of air. The weight loss up to 200°C (ranging from 1 to 10 wt.%, average 4 wt.%) may be attributed to the removal of any adsorbed water and lighter organics in the catalysts. The weight loss between 250 and 600°C may be attributed to the combustion of heavier organic residues (ethyl acetate-insoluble oils, tars andcoke referred to in this work as char for convenience) that had been deposited on the catalysts during reaction. The mass of char varied widely depending on the catalyst tested. The least amount of char, for the Ru/$Al_2O_3$ catalyst was only 1.3 wt.%. In contrast, the acidified zeolite (without metal catalyst) experienced severe char build-up totaling 65.6 wt.%. The TGA curves for some spent catalysts are presented in Figure 3-15. The TGA curves show that the $Al_2O_3$-supported catalyst did indeed exhibit very little carbon build-up (<2 wt%), while the zeolite-supported MoCoP catalysts resulted in a relatively larger amount of char deposition (~ 10 wt%).

The presence of P on the catalyst was found to have a beneficial effect on the amount of char deposited on the spent catalyst. The MoCo/$Al_2O_3$ catalyst experienced a build-up of 6.6 wt.% char compared to only 2.8 wt.% for the MoCoP/$Al_2O_3$ catalyst. This result confirms the findings of previous research and suggests the presence of small amounts of phosphorus in HDO catalysts may enhance resistance to coking (Yang et al., 2009).

As shown by the XRD spectra and TGA results, the deposition of carbon on the catalyst surfaces can be significant and may be the cause of catalyst deactivation even at lower levels. The presence of coke particles and heavy reside could coat the metal catalysts and also block the pores in the catalyst resulting in incomplete conversion of the glycerol and, consequently, incomplete hydrogen consumption.

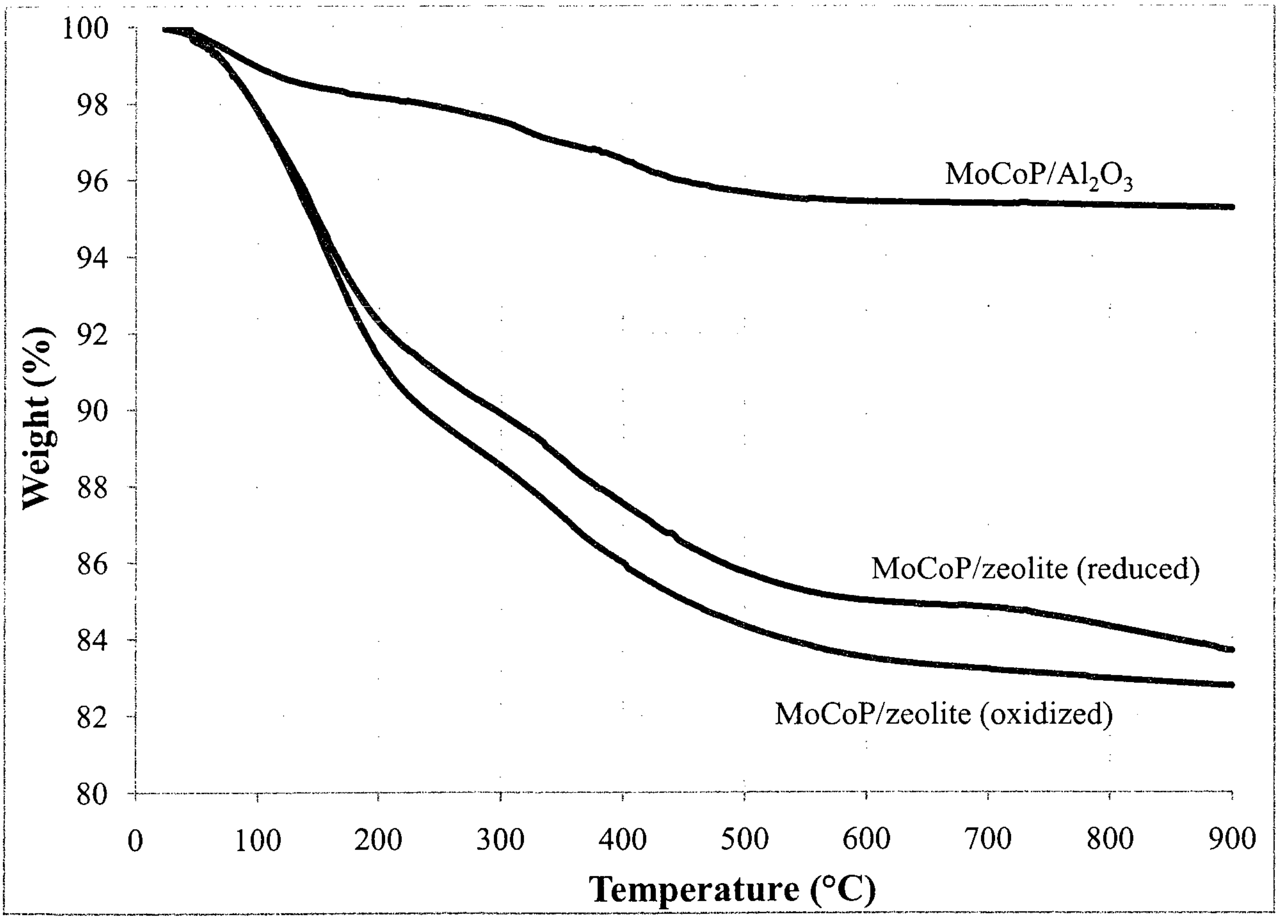


Figure 3-15. TGA analysis of some spent catalysts

### 3.4 Conclusions

In this study, the hydrodeoxygenation of glycerol in the presence of various catalysts was investigated. High yields of bio-oils with a HHV of ~30 MJ/kg were obtained by hydrodeoxygenation of glycerol in the presence of MoCoP/zeolite catalyst under a hydrogen atmosphere at 5.0 MPa initial pressure and reacted at a temperature of 300°C for 1 h. The results of the present study may be summarized as follows:

(1) Acid-supported catalysts are more effective for converting glycerol into bio-oil than either basic- or neutral-supported catalysts.

(2) Zeolite-supported MoCoP catalyst was found to be the most effective in the production of bio-oil from glycerol.

(3) Both reduction and sulfidation of the MoCoP/zeolite catalyst were found to have a marked negative effect on bio-oil yields.

(4) The presence of P in the catalyst reduced the amount of char deposited on the spent catalysts.

(5) GC/MS analysis revealed that the bio-oil produced by hydrodeoxygenation of glycerol is composed mainly of substituted phenols, ketones and to a lesser extent alcohols, ethers and cycloalkanes in the C6 to C9 range.

(6) The bio-oil produced has HHVs up to 33MJ/kg compared to the HHV of 16 MJ/kg for the glycerol feedstock indicating hydrodeoxygenation is a promising technique for the upgrading of glycerol into bio-oil/bio-crude with a significantly increased heating value.

# References

Alonso DM, Bond JQ, Serrano-Ruiz JC and Dumesic JA. Production of liquid hydrocarbon transportation fuels by oligomerization of biomass-derived C9 alkenes. *Green Chem.* **12** (2010) 992–999

Byrd, AJ et al., Hydrogen production from glycerol by reforming in supercritical water over Ru/$Al_2O_3$ catalyst. *Fuel* **87** (2008) 2956-2960.

Byambajav E, and Ohtsuka Y., *Appl. Catal.* A **252** (2003) 193-204.

Centeno A, Laurent E, Delmon B. Influence of the support of CoMo sulfide catalysts and of the addition of potassium and platinum on the catalytic performances for the hydrodeoxygenation of carbonyl, carboxyl, and guaiacol-type molecules. *J. Catal.* **154** (1995) 288-298.

Czernik S, Maggi R, Peacocke GVC. CPL Press, UK (2002) 141-145.

Dasari, MA. et al., Low-pressure hydrogenolysis of glycerol to propylene glycol, *Applied Catalysis A: General* **281** (2005) 225–231.

Elliott DC, *Energy Fuels* **21** (2007) 1792-1815.

EU Directive 2003/30/EC, The promotion of the use of biofuels and other renewable fuels for transport, 8 May 2003.

Iwata et al., Catalytic functionality of unsupported molybdenum sulfide catalysts prepared with different methods, *Catalysis Today* **45** (1998) 353-359

Klipcera T, Zdrazil M. Preparation of high activity MgO-supported Co-Mo and Ni-Mo sulfide hydrodesulfurization catalysts. *J. Catal.* **206** (2002) 314-320.

Lewis MJ, Kydd AR, Boorman MP, Van Rhyn HP. *Appl. Catal. A: Gen.* **84** (1992) 103.

Lopez RC, Lopez SG, Fierro GLJ, Lopez AA. *J. Catal.* **126** (1990) 8.

Marshall, AT and Haverkamp RG. Production of hydrogen by the electrochemical reforming of glycerol–water solutions in a PEM electrolysis cell *Int. J. of Hydrogen Energy* **33** (2008) 4649-4654.

Okkerse C, Van Bekkum H. Fossil to green. *Green Chem.* **1** (1999) 107-114.

Olson ES. Fine particle clay catalysts for coal liquefaction Quarterly Technical Report November 9, 1991 through February 8, 1992, DE-AC22-91PC90048, (1992).

Pater JPG, Jacobs PA and Martens JA. Oligomerization of Hex-1-ene over Acidic Aluminosilicate Zeolites, MCM-41, and Silica-Alumina Co-gel Catalysts: A Comparative Study *J. Catal.* **179** (1998) 477–482.

Patil RS, Uplane MD, Patil PS. Electrosynthesis of Electrochromic Molybdenum Oxide Thin Films with Rod-Like Features, *Int. J. Electrochem. Sci.* **3** (2008) 259 - 265

Pazé C, Gubitosa G, Orso Giacone S, Spoto G, Llabrés i Xamena FX, and Zecchina A. An XRD, FTIR and TPD investigation of NO2 surface adsorption sites of δ, γ Al2O3 and barium supported δ, γ Al2O3, *Topics in Catalysis* Vols. 30/31, July 2004

Radovic LR, Walker PL, Jenkins J. *Catal.* **82** (1983) 382-394.

Song C. Fuel processing for low-temperature and high-temperature fuel cells: challenges and opportunities for sustainable development in the 21st century. *Catal. Today* **77** (2002) 17-49.

Valliyappan, T. et al., Pyrolysis of glycerol for the production of hydrogen or syn gas. *Bioresour Technol.* **99** (2008) 4476–4483.

Yang Y, Gilbert A, Xu C Hydrodeoxygenation of bio-crude in supercritical hexane with sulfided CoMo and CoMoP catalysts supported on MgO: A model compound study using phenol, *Applied Catalysis A: General* **360** (2009) 242-249.

Yazdani, SS and Gonzalez, R, Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry *Current Opinion in Biotechnology* **18** (2007) 213–219.

Yokoyama S, Ogi T, Koguchi K, Nakamura E. *Liq. Fuels Technol.* **2** (1984) 115-163

Zdražil M. MgO-supported Mo, CoMo and NiMo sulfide hydrotreating catalysts. *Catal. Today* **86** (2003) 151-171.

Zhang, Y. et al., Inactivation of aldehyde dehydrogenase: A key factor for engineering 1,3-propanediol production by *Klebsiella pneumoniae. Metabolic Engineering* **8** (2006) 578–586.

# CHAPTER 4

# Hydrodeoxygenation of Glycerol into Bio-crude: Process Optimization

The optimum conditions for the hydrodeoxygenation (HDO) of glycerol were investigated using a micro-reactor in the presence of MoCoP/zeolite catalyst. The parameters which were investigated include initial hydrogen pressure, reaction temperature, residence time, and feedstock concentration. The liquid products were separated into water-soluble components and bio-oil by liquid-liquid extraction with water and ethyl acetate. The bio-oil, gaseous products, char and unreacted glycerol were quantified relative to the initial mass of glycerol feed. The composition of the bio-oil was determined by GC/MS. The optimum conditions for the hydrodeoxygenation of glycerol into bio-crude in the presence of MoCoP/zeolite catalyst were found to be: 300°C reaction temperature, 5 MPa initial hydrogen pressure, 60 min reaction time and 100% glycerol feed. While dilution of the glycerol feedstock with water had a negative effect on bio-oil yield, HDO of pure glycerol produced the highest bio-oil yield (40 wt.% at 300°C, 1 h and 5 MPa $H_2$). The amount of char deposited on the spent catalyst decreased with extended reaction time, increased reaction temperature, and elevated initial hydrogen pressure.

*Keywords*: bio-oil, bio-crude, glycerol, hydrodeoxygenation, MoCoP/zeolite catalyst

## 4.1 Introduction

Due to increasing concerns over greenhouse gas emissions and energy security, and with end of the fossil fuel era approaching, here has been a resurgence of interest in renewable bio-energy and bio-chemicals and the fossil-resource-based energy and chemical industries are expected to phase out gradually over the course of the 21st century (Okkerse and Van Bekkum, 1999). Many countries have legislation in place to promote the use of biomass energy and bio-fuels. For example, the European Union has set an objective to increase the market share of biomass-derived fuels in the transport sector to 5.75% by the end of 2010 (EU Directive 2003/30/EC). Concurrent with these initiatives, has been the increased production of bio-diesel from a variety of sources. Trans-esterification of fresh and spent cooking oils is one of the most common processes used to produce bio-diesel. The main by-product of trans-esterification is glycerol (approximately 1 kg of glycerol for every 9 kg of bio-diesel produced) (Dasari et al., 2005). The increased demand for bio-diesel has created a glut of glycerol (100,000 tonnes annually in the USA alone) and the cost of glycerol has decreased to a tenth of what it was just a few years ago (Yazdani and Gonzalez, 2007). Economically beneficial utilization of this glycerol by-product would greatly enhance biodiesel plant production economics. Much research is being conducted into the conversion of surplus glycerol into hydrogen (Marshal and Haverkamp, 2008; Valliyappan et al., 2005) and other value-added chemicals including ethanol (Yazdani and Gonzalez, 2007) and propylene glycol (Dasari et al., 2005; Zhang et al., 2008).

In our previously study (reported in Chapter 3) to screen catalysts for the hydrodeoxygenation (HDO) of glycerol feedstock to produce bio-crude oils at 300°C and initial hydrogen pressure of 5.0 MPa, the most effective catalyst for glycerol HDO was found to be oxidized form of MoCoP/zeolite which resulted in an average bio-oil yield of ~39 wt.%. In the present work, optimization of the HDO of glycerol was investigated using the zeolite-supported MoCoP catalyst at various temperatures between 275°C and 350°C under hydrogen at cold pressures varying from 2.5 to 10.0 MPa. Effects of reaction time and glycerol concentration on the glycerol conversion and bio-oil yield were also investigated in this study.

## 4.2 Experimental

### *4.2.1 Feedstock and Catalyst Preparation and Characterization*

The feedstock for these experiments was reagent grade glycerol obtained from Canadawide Scientific (99% purity), and was used as received or diluted with distilled water as required. The supported metal catalyst, 10%Mo-3%Co-2%P (MoCoP in short) was synthesized by successive incipient wetness impregnation. The catalyst support material (X-type zeolite) was reagent grade and dried at 105°C in air for a minimum of 8 h before use. The metal salts (ammonium molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) and cobalt (II) nitrate hexahydrate $(Co(NO_3)_2.6H_2O)$, and 86 wt.% phosphoric acid were A.C.S. reagent grade obtained from Sigma-Aldrich and used as received. The metal-impregnated catalyst was calcined at 550°C in air for 6 h. The cooled catalyst was crushed to a small (<300 μm) particle size before storage. The bulk elemental composition (molybdenum, cobalt and phosphorus contents) of the chosen catalyst was analyzed by inductively-coupled plasma-atomic emission spectroscopy (ICP-AES) and X-ray diffraction (XRD). The textural structure of the catalyst was analyzed by isothermal $N_2$ adsorption. The analyses of this catalyst are presented in Table 4-1.

Table 4-1. Elemental and textural analyses of the MoCoP/zeolite catalyst

| **Catalyst** | **Chemical compositions (wt.%)** | | | **BET surface area ($m^2/g$)** | **Porosity (cc/g)** | **Average pore (nm)** |
|---|---|---|---|---|---|---|
| | **Mo** | **Co** | **P** | | | |
| MoCoP/Zeolite | 6.5 | 2.3 | 1.5 | 2.58 | $8.20\times10^{-3}$ | 10.1 |

The XRD analysis was performed on the catalyst and the results are presented Figure 4-1. Multiple large peaks are present and represent the numerous crystallographic planes of the support material (X-zeolite), as can be seen in Figure 4-2 provided for reference.

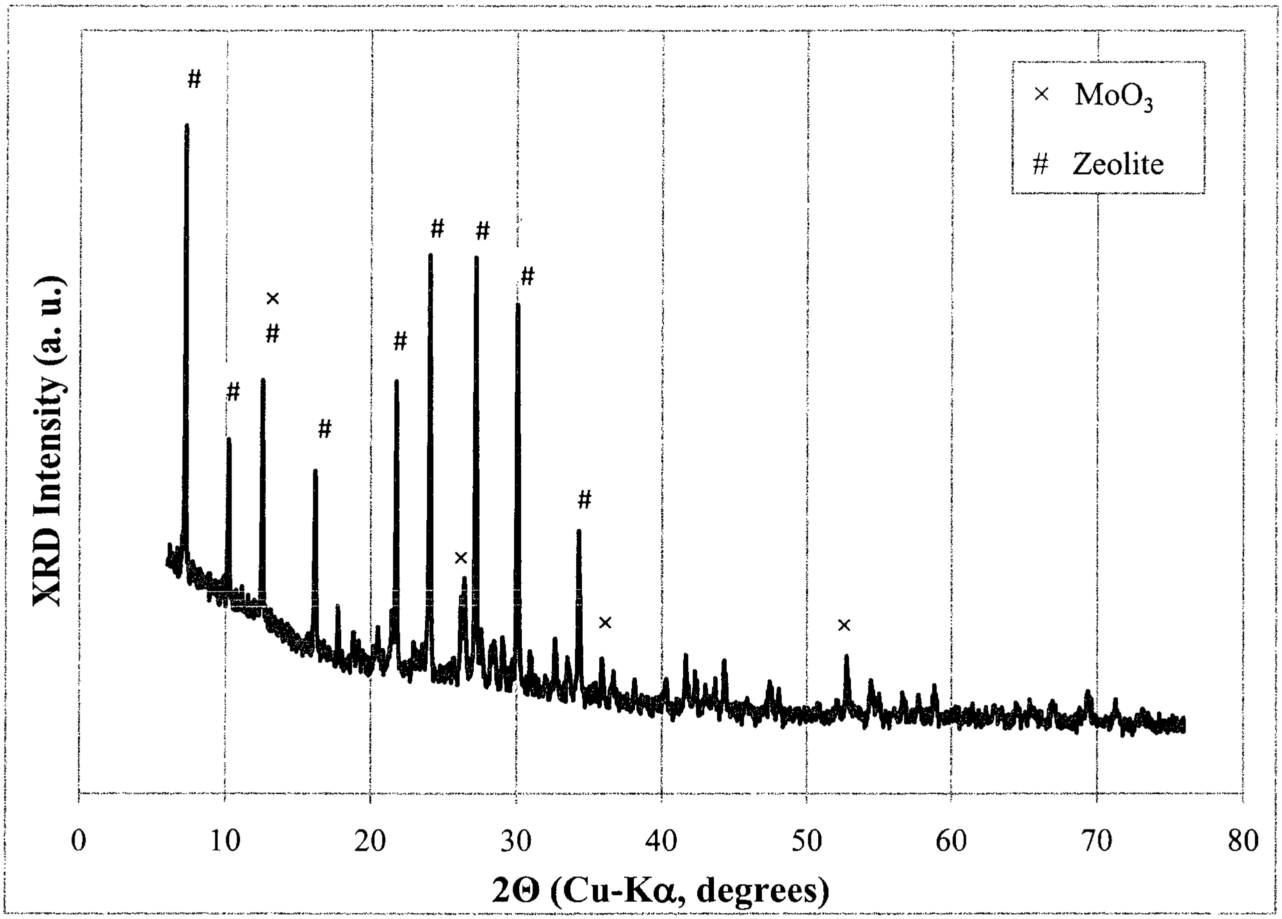


Figure 4-1. XRD spectrum of MoCoP/zeolite catalyst

The smaller peaks at 2Θ = 12.5°, 26.5°, 36° and 53° may be attributed to the presence of $MoO_3$ (Patil et al., 2008). The lack of strong metal oxide signals suggests that the metal species in this catalyst sample are very highly dispersed (Byambajav and Ohtsuka, 2003, Radovic et al., 1983).

Figure 4-2. Molecular sieve type X (www.grace.com)

### *4.2.2 Experimental Apparatus and Procedure*

All tests reported here were carried out in a high-pressure micro-reactor system whose details were given previously in Chapter 3. The micro-reactor used in this study, made of stainless steel (SS 316L), consisted of capped 5/8-inch Swagelok bulkhead unions and had an effective volume of 14 ml. In a typical run, 10 g of the feedstock (glycerol or diluted glycerol) was weighed into the reactor, followed by the addition of the 5 wt.% of the catalyst pulverized with a mortar and pestle to obtain very small particles. After sealing the reactor, the air inside the reactor was displaced by repetitive vacuuming and $N_2$-charging. Finally the reactor was charged with the required pressure (2.5-10 MPa) of ultra-pure hydrogen. Supported on a mechanical shaker (set at 100 rpm), the reactor was then rapidly submerged in a fluidized sand bath pre-heated to the desired temperature for the reaction (275°C - 350°C). After the predetermined reaction time (15-120 min) had elapsed, the reactor was removed from the sand bath and quenched in a water bath to stop the reactions. Once the reactor had cooled to room temperature, the gas inside was collected in a pre-evacuated gas cylinder with a fixed volume of 2.81 L. The pressure in the reactor was brought to ambient (required for analysis) by filling with $N_2$. The solid/liquid products were rinsed completely from the reactor into a beaker with reagent grade ethyl acetate and distilled water. The resulting mixture was filtered through a pre-weighed Whatman #5 filter paper to recover the spent catalyst and ethyl acetate insolubles (coke or char). The filtered solids were dried in air at 105°C overnight and allowed to cool in a desiccator before weighing. The filtrate was then decanted into a separatory funnel and the filter flask rinsed to ensure complete transfer of the bio-oil. After 30 s of vigorous shaking the liquids were allowed to separate overnight. After separation the aqueous layer was decanted and diluted to a known volume. A sample of the diluted solution was stored for later HPLC and DOC analysis. The remaining organic layer was decanted and diluted to a fixed volume. A sample of the organic phase was taken and stored for later GC/MS analysis. The organic solution was transferred to a pre-weighed round-bottomed flask and evaporated under vacuum at 60°C to remove the ethyl acetate. After evaporation the flask was allowed to cool in a dessicator before weighing, after which, if sufficient bio-oil was present, the viscosity of the oil was measured. The remaining bio-oil was rinsed completely from the flask into a sample vial with a minimum of acetone and stored at 4°C to minimize any condensation/polymerization reactions that might occur. Almost all the experimental runs were repeated a minimum of two times to ensure that the yields for runs under the same conditions were within 5% on one another.

### *4.2.3 Product Characterization*

As mentioned previously, the composition of the gaseous products was determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. The elemental composition (C, H and N) of the bio-oil was determined with a CEC (SCP) 240-XA elemental analyzer. The oxygen content was estimated by mass difference, assuming negligible content of sulfur in the products. The bio-oil products were also analyzed by GC/MS (Shimadzu QP2010S) with a SHRXI- 5MS column (30 m×0.25 mm×0.25 μm) and a temperature program of initial oven temperature 40°C, 10°C/min ramp to 200°C, hold for 2 min. Longer runs did not produce an improvement in the data. The glycerol content of the aqueous phases was determined by HPLC (Waters Breeze with a 1525 binary HPLC pump and 2414 RI detector. The Bio-rad Aminex HPX-87H column was maintained at 65°C using 0.005M $H_2SO_4$ in water as the eluant at a flow rate of 0.6 mL/min. The dispersion states and crystalline structures the fresh/spent catalyst were determined by X-ray diffraction (XRD) on a PANalytical X'Pert PRO X-ray diffractometer using Cu Kα radiation with a wavelength of 1.54187 Å.

## 4.3 Results and Discussion

The yield of bio-oil in the presence of MoCoP catalyst at 300°C, 5 MPa hydrogen, 1 h reaction time and 100% glycerol was very high (~40 wt%). The yield of char/heavy residue was found to be negligible for all of the conditions tested and will not be discussed.

### *4.3.1 Effect of Reaction Time*

The effect of reaction time on bio-oil yield followed the expected trend with bio-oil yields increasing with longer reaction time and then levelling off at a maximum bio-oil yield as can be seen in Figure 4-3. At 15 min the yield of bio-oil was 12.3 wt.%, while the yield increased to 17.1 wt.% at 30 min, and 32.0 wt.% at 45 min, and reached the maximum oil yield of 40 wt.% at 1 h reaction time. Further increasing the reaction time from 60 min to 120 min did not increase the bio-oil yield further. An increase in the reaction time from 15 min up to 60 min decreased the unreacted glycerol, or in other words, increased the glycerol conversion from 60% to 90%. These results suggest that 60 min is likely the optimum reaction time under for the present glycerol HDO process, which is consistent with the reaction conditions used for the catalysts screening in the previous chapter. In fact, the oil yields decreased slightly, although there was more variation in these later runs as can be seen by the error bars. The consumption of hydrogen generally followed the trends in bio-oil yield, increasing with higher bio-oil production indicating that hydrogen was consumed. The decrease in hydrogen consumption after 45 min may be due to the production of hydrogen via the reforming reactions of the bio-oil products by the water produced in the HDO process. The char yield in all tests was constantly low at ~0.4 wt.%.

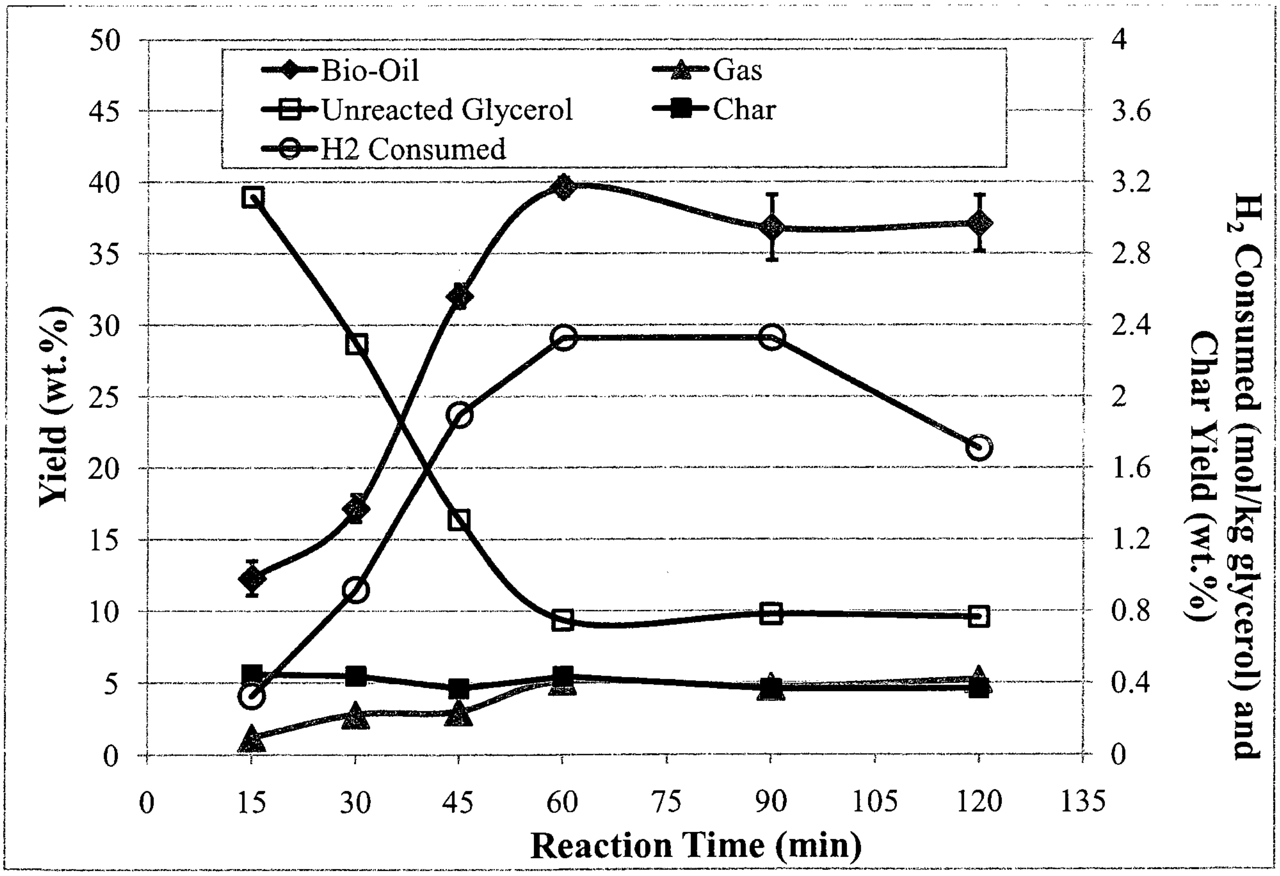


Figure 4-3. Effect of reaction time on product yields (300°C, 5 MPa $H_2$, 100% glycerol)

### *4.3.2 Effect of Reaction Temperature*

The dependency of various product yields on reaction temperature is presented in Figure 4-4. The char yields were negligibly low (<0.5 wt%) for all temperatures. Gas yields generally increased with increasing reaction temperatures, from almost 0 wt% at 275°C to approximately 8 wt% at 350°C. The higher temperatures can facilitate the cracking of any condensed product into gaseous products. This can also be explained by the enhanced reforming reaction of the feedstock or the HDO products by the water (a byproduct in the HDO process), to produce gaseous products of hydrogen and $CO/CO_2$. The newly formed hydrogen might account for the declined hydrogen consumption at higher temperatures, as displayed in Figure 4-4. The bio-oil yield at 275°C was very low at 1.7 wt.%. The oil yield increased drastically to 40 wt% as the

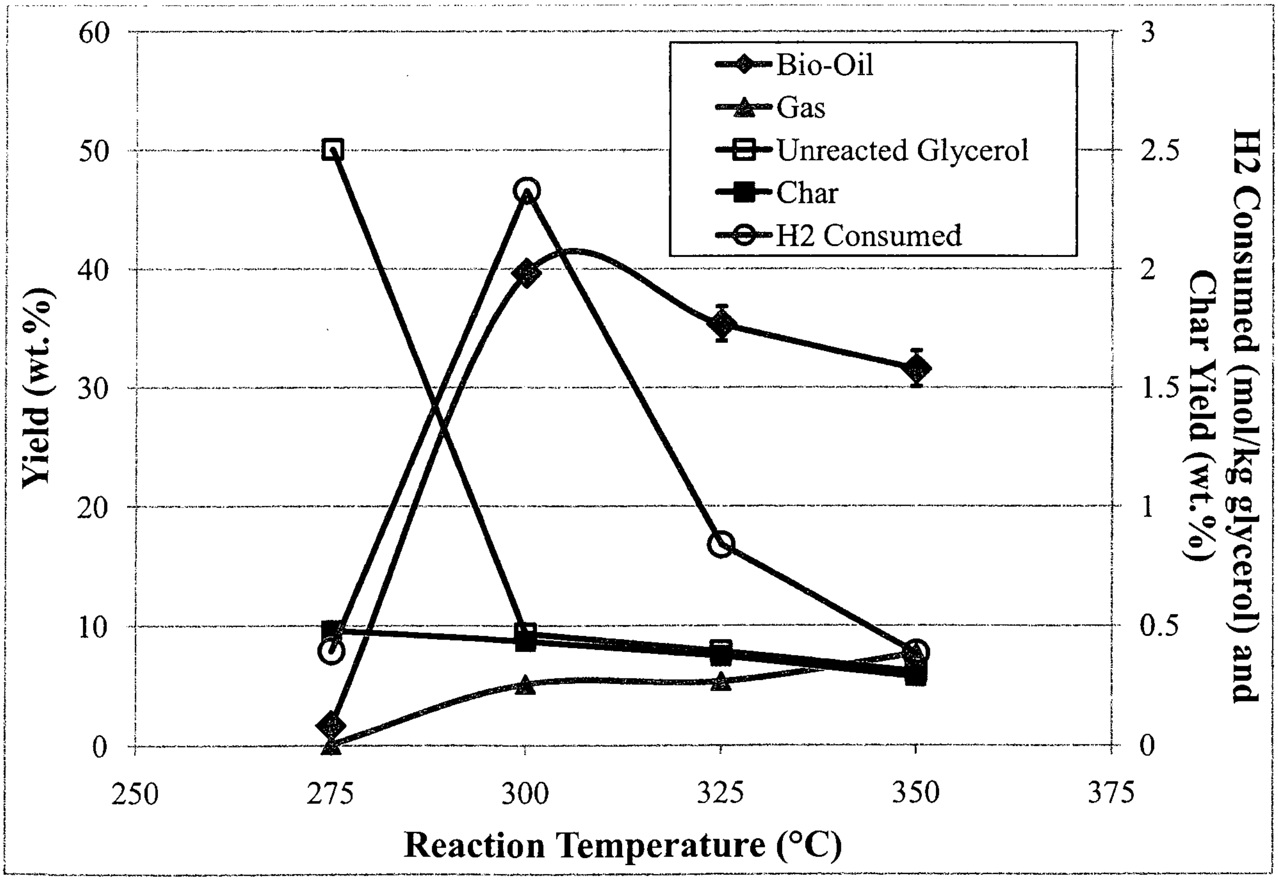


Figure 4-4. Effect of reaction temperature on product yields (1 h, 5 MPa $H_2$, 100% glycerol)

reaction temperature increased from 275°C to 300°C, accompanied by a marked decrease in the % of unreacted glycerol (from 50% to 10%). Surprisingly, HDO at temperatures higher than 300°C did not increase bio-oil yields, but led to a decrease in bio-oil yield. Some explanations are discussed as follows. The HDO of glycerol process involves oligomerization/polymerization and de-oxygenation reactions. Oligomerization/polymerization is an exothermic process, thermodynamically favorable at lower temperatures. The formation of bio-oil in the reaction system can be partially attributed to the oligomerization/polymerization of the HDO intermediates, followed by HDO of the oligomers. Thus, as the temperature increases higher than 300°C, oligomerization/polymerization is thermodynamically inhibited and results in declined oil yields. Moreover, the oligomer HDO reactions, enhanced at an elevated temperature, could also lead to a reduction in bio-oil yields. The enhanced HDO reactions at a higher temperature may be evidenced by the reduced oxygen contents of the bio-oil products, as shown in Table 4-2.

Table 4-2. Elemental compositions of bio-oils obtained from HDO of glycerol at various temperatures (5 MPa $H_2$, 60 min).

| **Reaction** | **Elemental Composition (wt.%)** | | | | **HHV** (2) |
|---|---|---|---|---|---|
| **Temperature (°C)** | **C** | **H** | **N** | **O** (1) | **(MJ/kg)** |
| 350 | 72.5 | 7.6 | 0.0 | 19.9 | 32 |
| 325 | 70.3 | 7.0 | 0.0 | 22.7 | 30 |
| 300 | 74.0 | 7.5 | 0.0 | 18.5 | 33 |
| 275 | 58.3 | 7.7 | 0.0 | 34.0 | 25 |

[1] By difference and assuming that the sulfur content is negligible;

[2] Higher heating value (HHV) calculated by the Dulong Formula, i.e., HHV (MJ/kg) = 0.3383C + 1.422 (H – O/8)

In terms of the yield of bio-oil, these results suggest that 300°C appeared to be the optimum reaction temperature under for the present glycerol HDO process, which is consistent with the reaction conditions used for the catalysts screening in the previous chapter.

### *4.3.3 Effect of Initial Hydrogen Pressure*

The effect of initial hydrogen pressure on the various product yields is presented in Figure 4-5. The yield of bio-oil at 2.5 MPa hydrogen was 15 wt.%. This value more than doubled to ~40 wt.% at 5 MPa hydrogen, while the consumption of hydrogen also increased by ~50% and the percentage of unreacted glycerol decreased greatly from 35 wt% (2.5 MPa $H_2$) to approximately 10 wt% (5.0 MPa $H_2$). Increasing initial hydrogen pressure from2.5 MPa to 5.0 MPa also led to an increase in gas yield from 1.6 wt.% to 5.1 wt.%. The experiment conducted under 5 MPa nitrogen instead of hydrogen resulted in much lower bio-oil yield (12.6 wt.%) compared to the 5 MPa hydrogen runs (~40 wt.%), accompanied by a much higher % of

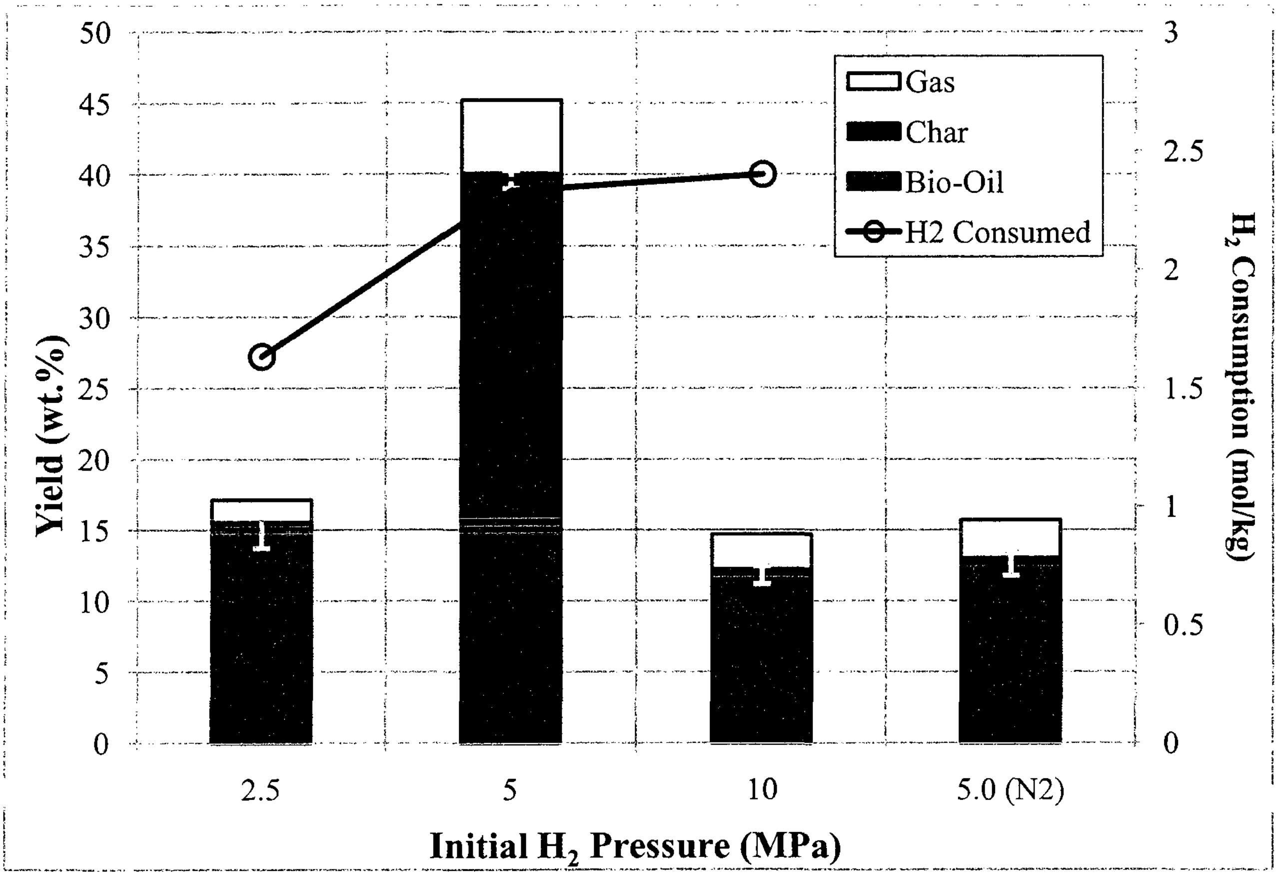


Figure 4-5. Effect of initial hydrogen pressure on product yields (60 min, 300°C, 100% glycerol)

unreacted glycerol, as clearly displayed in Figure 4-5. The gasification of glycerol under $N_2$ was approximately half that found during the 5 MPa $H_2$ experiment. The Micro-GC analysis of the gaseous products from the test under $N_2$ revealed significant formation of $H_2$ at 0.4 mol/kg of glycerol in the process, which indicated the presence of reforming reactions between the feedstock or the de-oxygenation products and the water by-product in the process.

Surprisingly, increasing the initial hydrogen pressure further to 10 MPa resulted in a decrease in bio-oil yield, possibly due to the fact that, with the gases that are produced, this is a volume-increasing reaction and higher pressure inhibits bio-oil production. Even though the bio-oil yield was low, the consumption of hydrogen increased slightly, possibly indicating the production of higher quality oil.

### *4.3.4 Effects of Glycerol Concentration and Addition of Other Solvent*

The effects of glycerol concentration (diluted by distilled water) on the yield of bio-oil are presented in Figure 4-6. As can be seen, in all operations the yields of gaseous products were low (<5 wt%) and the formation of char was negligible (<0.5 wt%). The dilution of glycerol had a marked negative effect on bio-oil yield, decreasing from 40 wt.% with 100% glycerol to 24 wt.% and 7.6 wt.% with 80 wt.% and 50 wt.% glycerol, respectively. These results are relative to the amount of glycerol added, not the mass of diluted feed. As a result of the dilution, hydrogen consumption decreased and the % of unreacted glycerol increased with increasing the water content of the glycerol feedstock. The above results may be explained by the reaction kinetics and equilibrium shift for the following simplified glycerol HDO reaction (assuming an HDO efficiency of 100%):

$$n\,C_3H_8O_3 + 2n\,H_2 \leftrightarrow n\,(C_3H_6) + 3n\,H_2O \qquad (1)$$

As is clearly shown in the above reaction, dilution of the glycerol reactant ($C_3H_8O_3$), or reduction in the reactant concentration, would decrease the reaction rate. Furthermore, the addition of water (the reaction by-product) would cause an equilibrium shift to favour the reverse reaction. As a consequence, dilution of glycerol feedstock would decrease the bio-oil yields, as was evidenced by the results in Figure 4-6. HDO of 50% glycerol diluted in a non-polar hydrocarbon solvent (heptane) was found to be more effective than that in water. As can be seen, the yield of bio-oil in the presence of 50% heptane was over 4 times higher than when diluted 50% with water (~32 wt.% vs. 7.6 wt.%) indicating that the reaction had proceeded to a greater extent in the presence of the hydrocarbon solvent. The superior performance of heptane

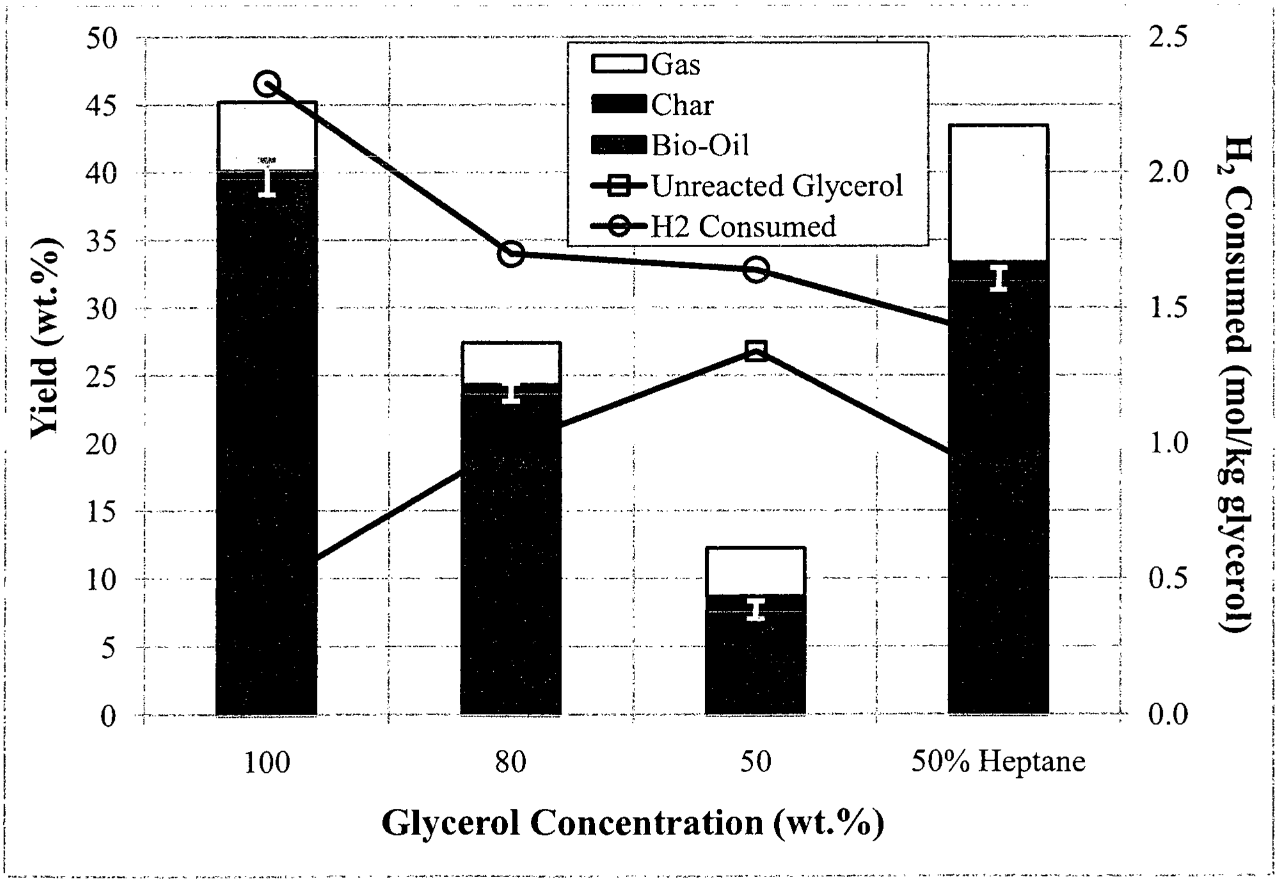


Figure 4-6. Effect of glycerol concentration & solvent effect on product yields (60 min, 5 MPa $H_2$, 300°C)

compared to water in the reaction system may be explained as follows: heptane, as a non-polar solvent, has a better solubility for the reaction products and hence can increase the driving force of the reaction. The results of this section thus demonstrate that pure glycerol would be the best feedstock for the bio-oil production by HDO. HDO of crude glycerol would lead to a lower bio-oil yield due to the presence of water, but the oil yield might be improved by addition of some suitable non-polar solvents, which will be investigated further in future work.

### *4.3.5 Chemical Analysis of the Glycerol HDO Products*

Carbon balances were calculated in order to evaluate the material balance of the HDO operations. The carbon compositions of the HDO products (bio-oils and the aqueous products) were analyzed with an elemental analyzer and DOC. The carbon content of the spent catalyst was determined indirectly by TGA, and the carbon content of the gaseous products was obtained by GC-TCD. Carbon recovery in the products was defined by the percentage of the moles of carbon in the products in relation to the moles of carbon originally present in the glycerol prior to hydrodeoxygenation. The results of the carbon balances, calculated by summing the carbon recovery for all of the products, are presented in Table 4-3. As discussed previously in Chapter 3, the aqueous carbon recovery is the greatest source of error in these calculations. The highlighted values in particular do not agree with the amounts of unreacted glycerol as determined by HPLC.

Table 4-3. Carbon recovery in the products of the HDO of glycerol with MoCoP/zeolite catalyst

| **Reaction** | **Carbon Recovery in Products (%)** | | | | **Carbon** |
|---|---|---|---|---|---|
| **Condition** | **Bio-Oil** | **Aqueous** | **Char** | **Gas** | **Balance (%)** |
| 350°C | 57.4 | 37.0 | 0.7 | 16.7 | 111.9 |
| 325°C | 63.4 | 49.0 | 0.9 | 11.8 | 125.1 |
| 275°C | 3.0 | 92.1 | 1.2 | 0.3 | 96.7 |
| 120 min | 71.1 | 37.5 | 0.9 | 8.7 | 118.3 |
| 90 min | 65.3 | 38.5 | 0.9 | 9.9 | 114.6 |
| 45 min | 58.4 | 49.0 | 1.0 | 6.9 | 115.3 |

Table 4-3. Continued

| Reaction Condition | Carbon Recovery in Products (%) | | | | Carbon Balance (%) |
|---|---|---|---|---|---|
| | Bio-Oil | Aqueous | Char | Gas | |
| 30 min | 30.4 | 50.2 | 1.1 | 7.9 | 89.7 |
| 15 min | 21.3 | 55.2 | 1.0 | 3.0 | 80.6 |
| 50% Glycerol | 6.7 | 85.9 | 1.3 | 2.5 | 96.4 |
| 80% Glycerol | 31.3 | 59.9 | 1.2 | 2.5 | 95.0 |
| 50% heptane | 26.3 | 68.2 | 1.6 | 5.4 | 101.4 |
| 10 MPa $H_2$ | 18.6 | 64.9 | 1.1 | 5.7 | 90.3 |

The chemical composition of the bio-oil products from the hydrodeoxygenation of glycerol under different conditions (reaction time, reaction temperature, hydrogen pressure and feed concentration) was analyzed by GC/MS. The results of these analyses are presented in Figures 4-7 through 4-9. Figure 4-7 illustrates the similarity in the composition of the bio-oils from different reaction times.

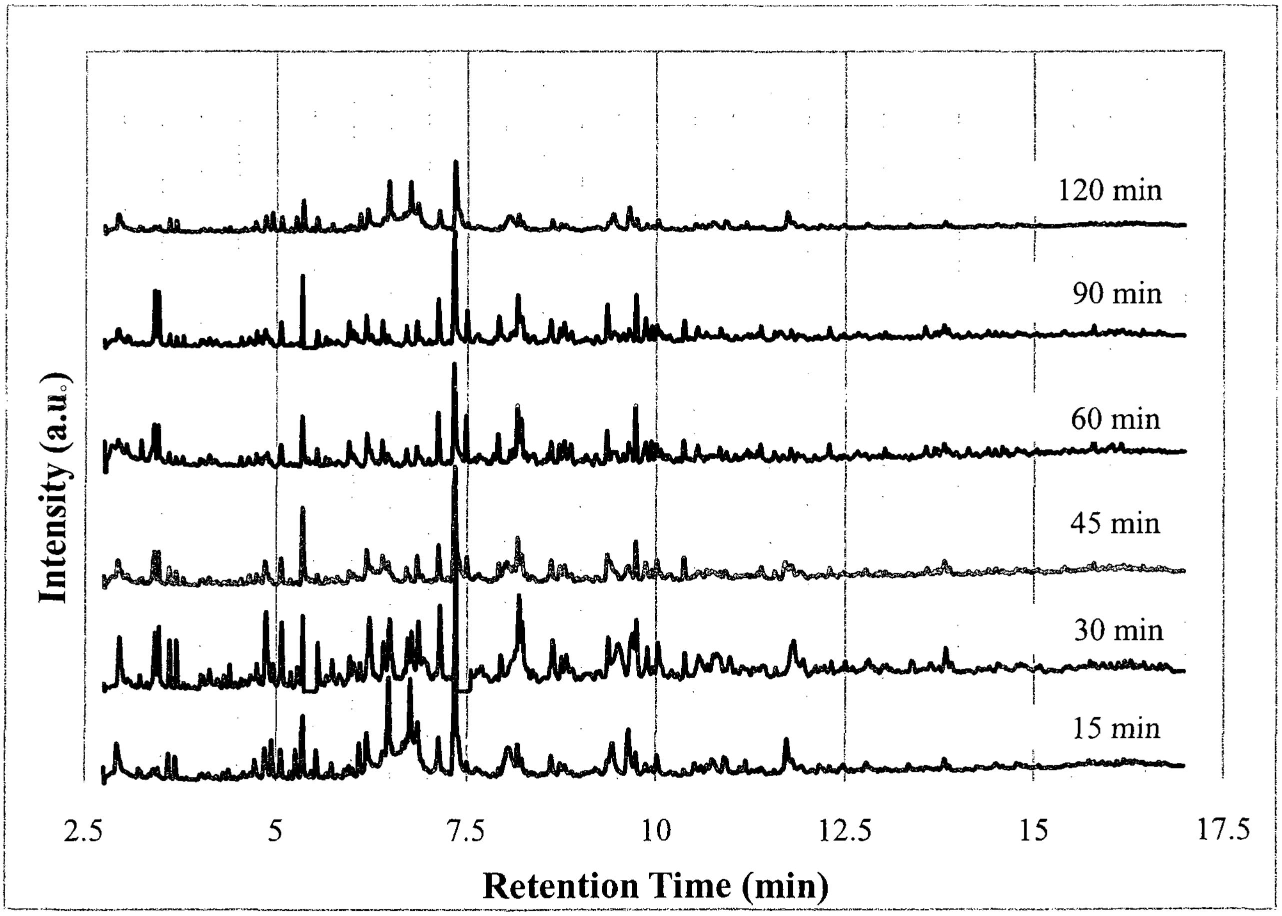


Figure 4-7. GC/MS chromatograms for bio-oils from different reaction times (300°C, 5MPa $H_2$, 100% glycerol)

An abridged list of the compounds found in the bio-oils at different reaction times is presented in Table 4-4. The area percent values are with reference to the individual chromatograms and may be used to show qualitatively the relative abundance of the compounds in each sample.

Table 4-4. GC/MS analysis results for bio-oils from different reaction times (300°C, 5MPa $H_2$, 100% glycerol)

| **RT** | **Compound** | **15 min** | **30 min** | **45 min** | **60min** | **90 min** |
|---|---|---|---|---|---|---|
| 2.938 | 1,2-PROPANEDIOL | 1.69 | 2.34 | 1.47 |  | 0.56 |
| 3.412 | 3-HEXANONE |  | 1.69 | 1.96 | 2.06 | 1.3 |
| 3.458 | 2-HEXANONE | 0.86 | 1.53 | 1.37 | 1.46 | 1.3 |
| 4.854 | 2-HYDROXY-3-HEXANONE | 1.66 | 4.03 | 2.49 |  |  |
| 5.06 | 2-METHYL-2-CYCLOPENTEN-1-ONE | 0.98 | 2.17 | 1.73 | 1.06 |  |
| 5.345 | 2,5-HEXANEDIONE | 2.17 | 1.35 | 4.33 | 2.54 | 3.88 |
| 5.957 | 3-METHYL-2-CYCLOPENTEN-1-ONE | 0.43 | 1.23 | 0.73 | 1.5 | 1.78 |
| 6.187 | PHENOL | 3.03 | 4.24 | 3.53 | 2.23 | 3.48 |
| 6.395 | 3,4-DIMETHYL-2-CYCLOPENTEN-1-ONE |  | 2.6 | 4.11 | 1.83 | 1.14 |
| 6.472 | 2-ETHYL-1,3-DIOXOLANE-4-METHANOL | 12.28 | 6.12 |  |  |  |
| 6.664 | 4-METHYL-1,3-DIOXOLAN-2-ONE | 3.8 | 0.78 |  |  |  |
| 6.708 | 2-METHYL-2,5-CYCLOHEXADIENE-1,4-DIONE |  | 1.55 | 1.31 | 1.06 |  |
| 6.854 | 5-ETHYLDIHYDRO-5-METHYL-2(3H)-FURANONE | 4.43 | 2.82 |  | 1.33 |  |
| 7.126 | 2,3-DIMETHYL-2-CYCLOPENTEN-1-ONE | 2.35 | 2.93 | 3.19 | 3.27 | 3.21 |
| 7.337 | 2-METHYL PHENOL | 7.67 | *sat.* | 9.3 | 7.9 | 12.69 |
| 7.496 | 2,3,4-TRIMETHYL-2-CYCLOPENTEN-1-ONE | 0.35 |  | 2.06 | 4.24 | 2.8 |
| 7.62 | 3-METHYL PHENOL |  |  |  | 1.71 | 1.45 |
| 8.032 | 1,2,3-PROPANETRIOL 1-ACETATE | 3.82 | 2.07 | 2.41 |  |  |
| 8.175 | 2,6-DIMETHYLPHENOL | 1.58 | 6.06 | 3.77 | 5.4 | 5.5 |
| 8.227 | 2-METHYL BENZOFURAN | 0.56 | 2.97 | 1.84 | 2.56 | 1.55 |
| 8.616 | 2-ETHYLPHENOL | 0.75 | 2 | 1.43 | 1.34 | 2.27 |
| 9.354 | 2-ETHYL-5-METHYL PHENOL | 0.62 | 2.19 | 3.84 | 2.03 | 1.6 |
| 9.424 | 1,2-ETHANEDIOL DIPROPANOATE | 2.24 | 4.85 | 0.67 |  |  |
| 9.636 | 1,2-BENZENEDIOL | 2.86 | 3.58 | 2.42 |  | 1.25 |
| 9.734 | 4,7-DIMETHYL BENZOFURAN | 0.76 | 2.32 | 2.03 | 2.7 | 2.38 |
| 9.862 | 2-PROPYL PHENOL | 0.56 | 1.74 | 1.64 | 1.98 | 2.43 |
| 10.013 | 2-METHYL-2-INDANOL | 1.29 | 2.35 | 1.45 | 1.17 | 1.83 |
| 10.371 | 1-(2-HYDROXY-5-METHYLPHENYL)-ETHANONE |  | 1.09 | 1.17 | 1.01 | 2.27 |
| 11.7 | 2-METHYL-1,4-BENZENEDIOL | 1.66 | 6.23 | 2.00 |  | 6.35 |
| **Total Area %** |  | **61.42** | **72.83** | **62.25** | **50.38** | **61.02** |

The compounds in the table above were chosen to show the most abundant compounds common to all of the bio-oils produced at different reaction times in comparison to the highest yielding condition at 60 min. The results of the 120 min run are omitted for brevity. As can be seen, the majority of the bio-oils is made up of substituted phenols, ketones and diones as well as a few diols. While the relative abundances of the individual compounds vary from bio-oil to bio-oil, the general composition is relatively consistent.

The same can be said for the three of the four bio-oils presented in Figure 4-8. As can be seen in the figure, the oils from runs at 300°C, 325°C, and 350°C are all very similar and only vary in the strength of response at the various retention times. This indicates that after 300°C the composition of the oils does not change appreciably. The bio-oil at 275°C, however, shows that a considerable amount of unreacted glycerol is present. This was confirmed by the HPLC analysis, indicating that the glycerol conversion was 50% at 275°C, compared to >90% at temperatures ≥

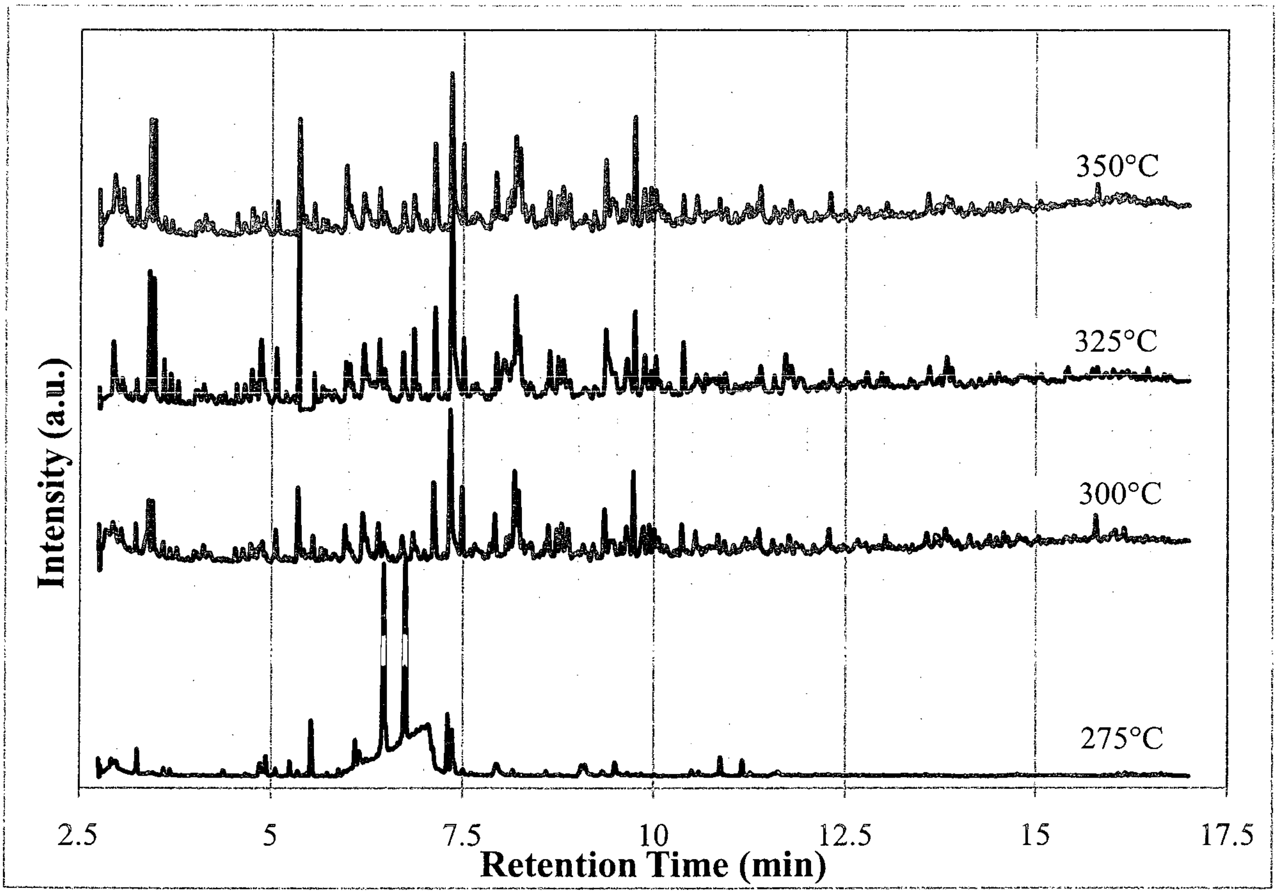


Figure 4-8. GC/MS chromatograms for bio-oils from different reaction temperatures (60 min, 5 MPa $H_2$, 100% glycerol)

300°C (Figure 4-4). Other than glycerol, phenol, 2-methyl phenol, 2,2-dimethyl-1,3-dioxolane-4-methanol and 2-ethyl-1,3-dioxolane-4-methanol are present in the 275°C bio-oil, and they are also present in the other bio-oils from different temperatures.

Figure 4-9 illustrates the differences in bio-oil composition for experiments conducted under different hydrogen pressures and also a nitrogen atmosphere. The chromatogram of the bio-oil produced under a nitrogen atmosphere shows that the oil produced under a $N_2$ atmosphere is much simpler in composition compared to the oils produced under a hydrogen atmosphere. Its chromatogram does reveal the presence of 6 to 8-carbon ketones and diones as well as

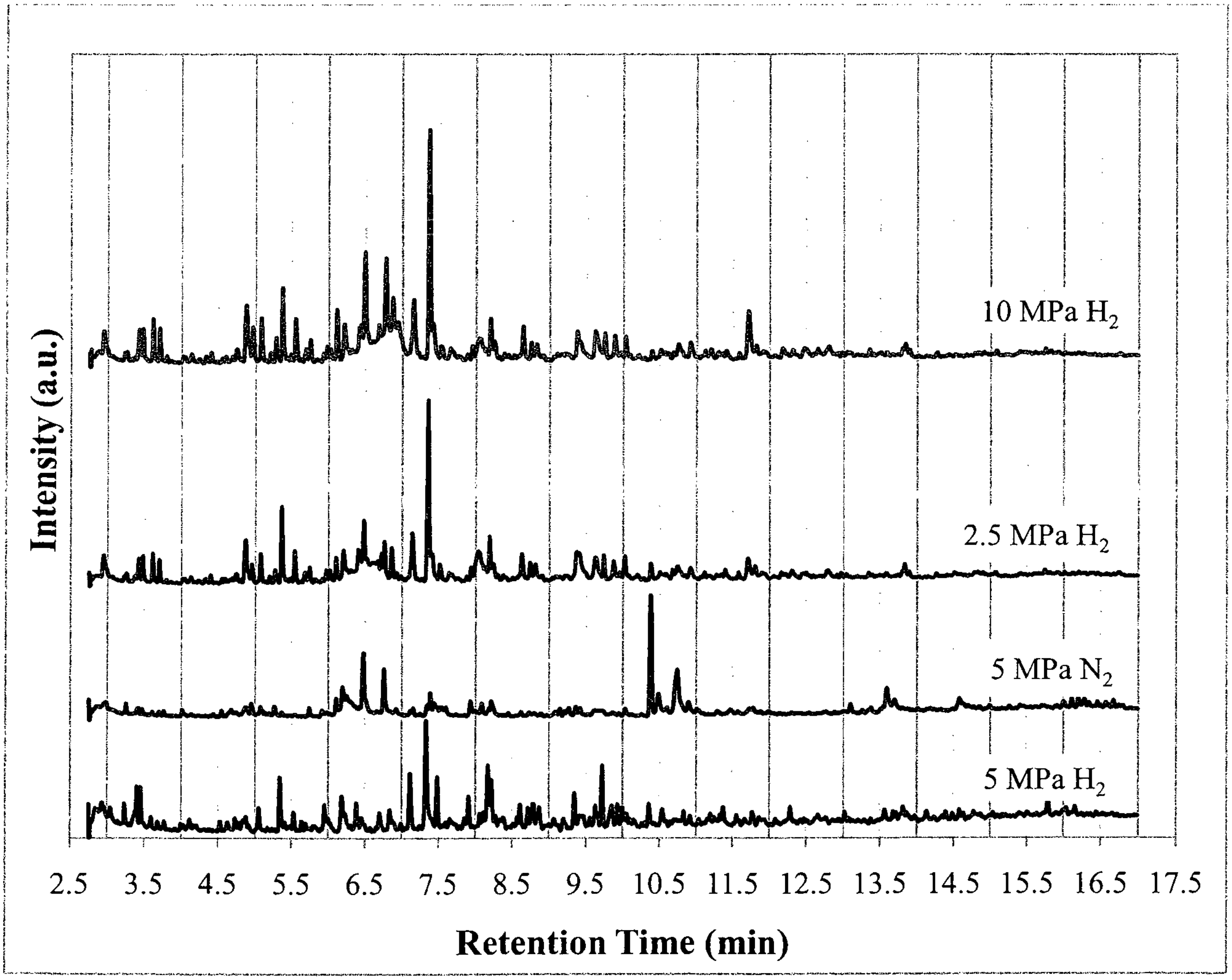


Figure 4-9. GC/MS chromatograms for bio-oils from different atmospheres (300°C, 1h, 100% glycerol)

substituted phenols such as 2-methyl phenol, 2,6-dimethyl phenol, and 2-ethyl phenol but with reduced quantity compared to the other oils. Surprisingly, the 10 MPa condition reveals the presence of unreacted glycerol, which was confirmed by HPLC analysis of the aqueous products. Figure 4-10 presents the GC/MS results for the bio-oils collected for the runs conducted with different concentrations of glycerol. The most obvious result is that the diluted glycerol runs, which resulted in poor bio-oil yields, produced bio-oils containing a significant amount of unreacted glycerol. This can be evidenced by the high percentage of unreacted glycerol as was evidenced by the HPLC analysis (Figure 4-6). Other than the unreacted glycerol content, the composition of all of these oils is consistent with the bio-oils analyzed previously, containing, for

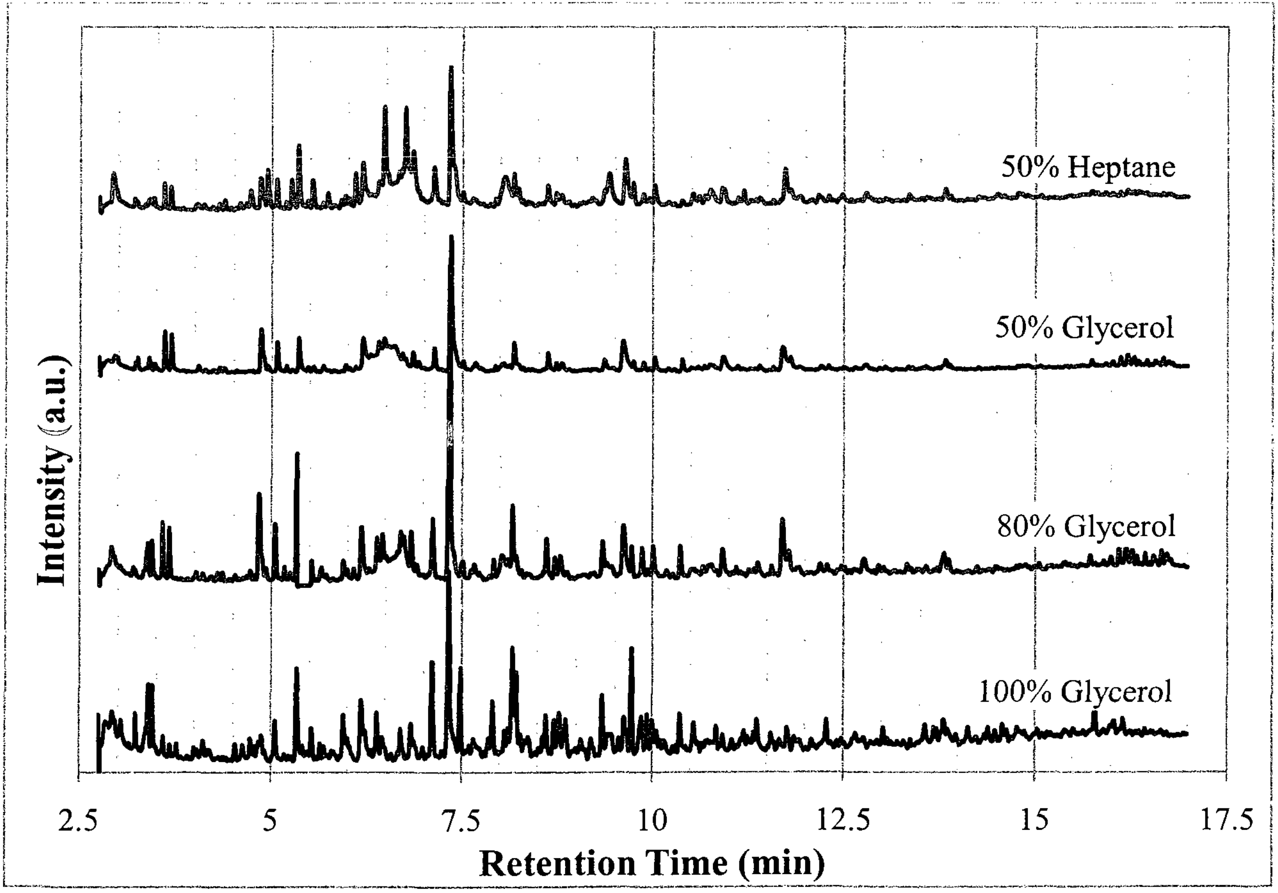


Figure 4-10. GC/MS chromatograms for bio-oils from different glycerol concentrations (300°C, 5 MPa $H_2$, 1h)

the most part, substituted phenols and ketones in the C6-C9 range. The presence of heptane does not seem to have affected the bio-oil composition.

### *4.3.6 Characterization of the Spent Catalysts*

As was stated previously the fresh (as-synthesized) catalyst was characterized by powder X-ray diffraction (XRD). The spent catalyst was collected after each run for later TGA analysis. Selected spent catalysts were also analyzed by XRD in order to determine the evolution of the metal oxides during the HDO process. Figure 4-11 presents XRD spectra of fresh and spent MoCoP/zeolite catalyst after HDO of pure glycerol at 300°C under 5 MPa $H_2$ for 1h.

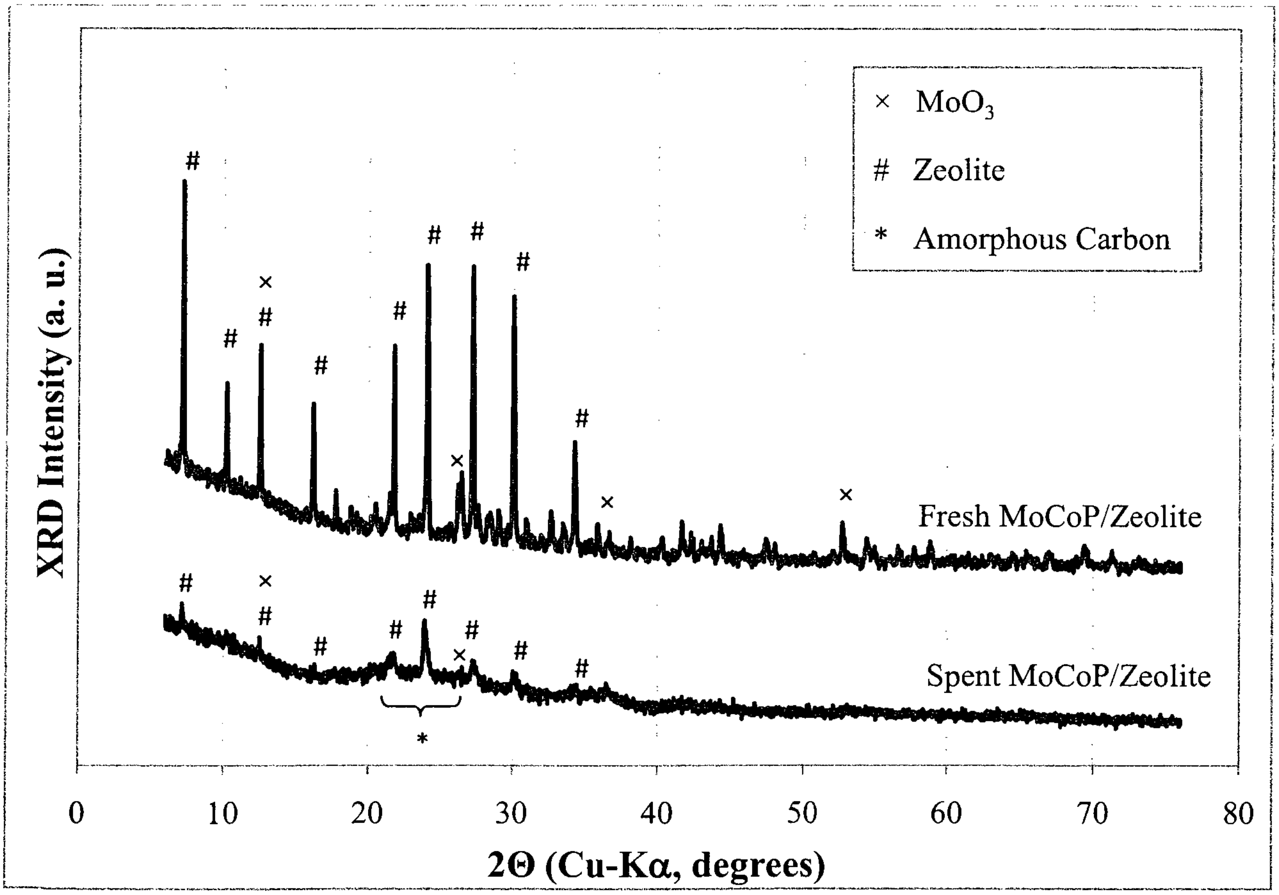


Figure 4-11. Comparison of the XRD patterns for fresh and spent MoCoP/zeolite catalyst after HDO of pure glycerol at 300°C under 5 MPa $H_2$ for 60 min

The most striking difference between the fresh and spent catalysts is the reduction of the signals attributable to the zeolite support. In addition, the peaks due to $MoO_3$ are also greatly diminished or eliminated. The reason for this is most likely due to the masking effects of the deposition of heavy residue and coke on the surface of the catalyst. This may be evident from the broad peak centered on $2\Theta = 24°$ which is due to the presence of amorphous carbon.

In order to examine the extent of solid residue/coke formation during the hydrodeoxygenation of glycerol under different conditions, TGA analysis of was performed on the spent catalysts. The TGA profiles of the spent catalysts under the different conditions tested are presented in Figures 4-12 through 4-14. The TGA profiles were collected by heating the spent catalysts at 30 K/min from room temperature up to 900ºC in 40 mL/min flow of air. The weight loss up to 200°C (average of 6 wt.% for all of the catalyst) can be attributed to the removal of the water and lighter organics in the catalysts. The remaining weight loss can be attributed to the combustion of heavier residual oils, coke and tar deposited on the catalysts. The amount of char on the catalysts was then calculated by mass difference between 200°C and 900°C. The TGA results as seen in Figure 4-12 reveal that HDO of glycerol at a higher temperature results in less severe coke deposition as was discussed previously in Figure 4.4, although the maximum difference between the 275°C and 350°C runs is only in the range of 5.5 wt.%.

The TGA curves in Figure 4-13 show that, as a general trend, the amount of char deposited on the spent catalyst decreases with extended reaction time, although the maximum difference is only in the range of 3 wt.%. This finding is consistent with the results of char yields vs. reaction time as discussed previously in Figure 4-3 and could be due to reaction between the coke and

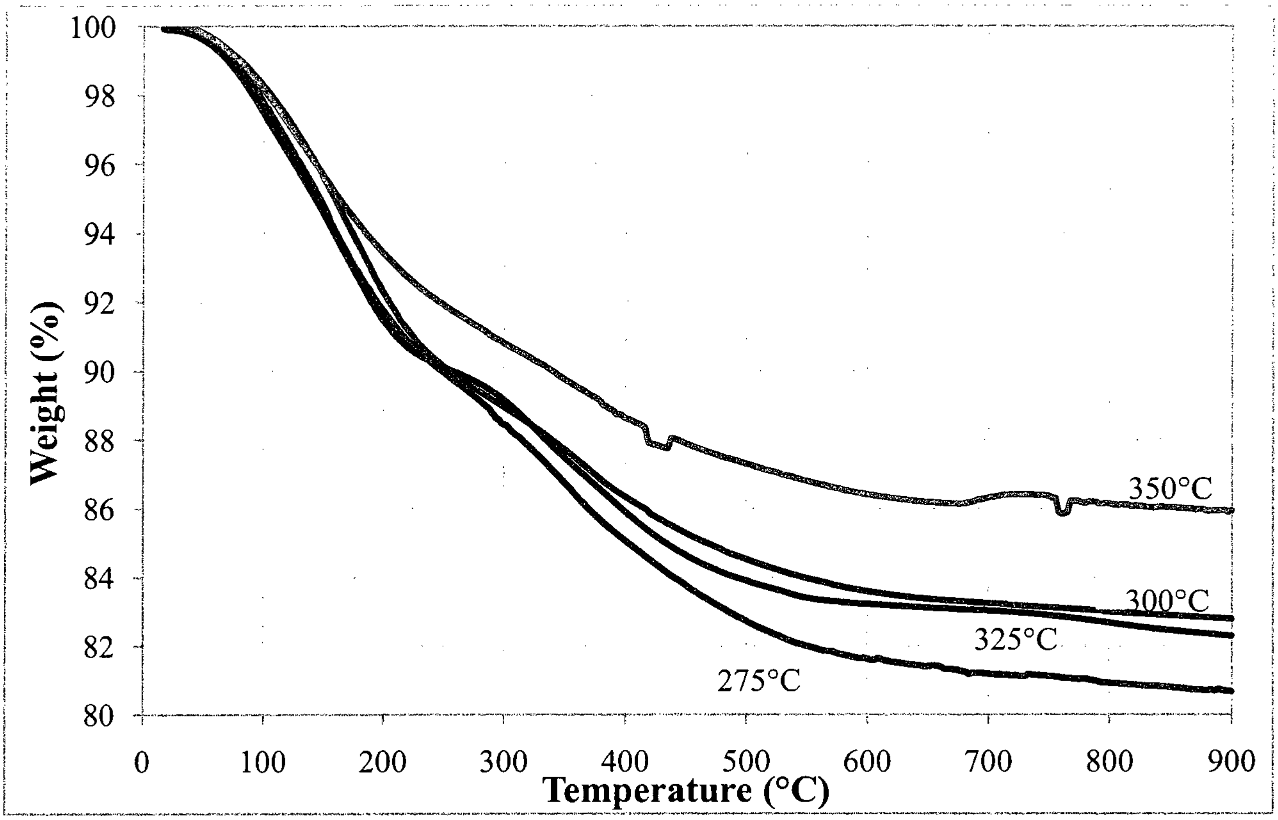


Figure 4-12. TGA comparison of spent MoCoP/zeolite catalyst at different reaction temperatures

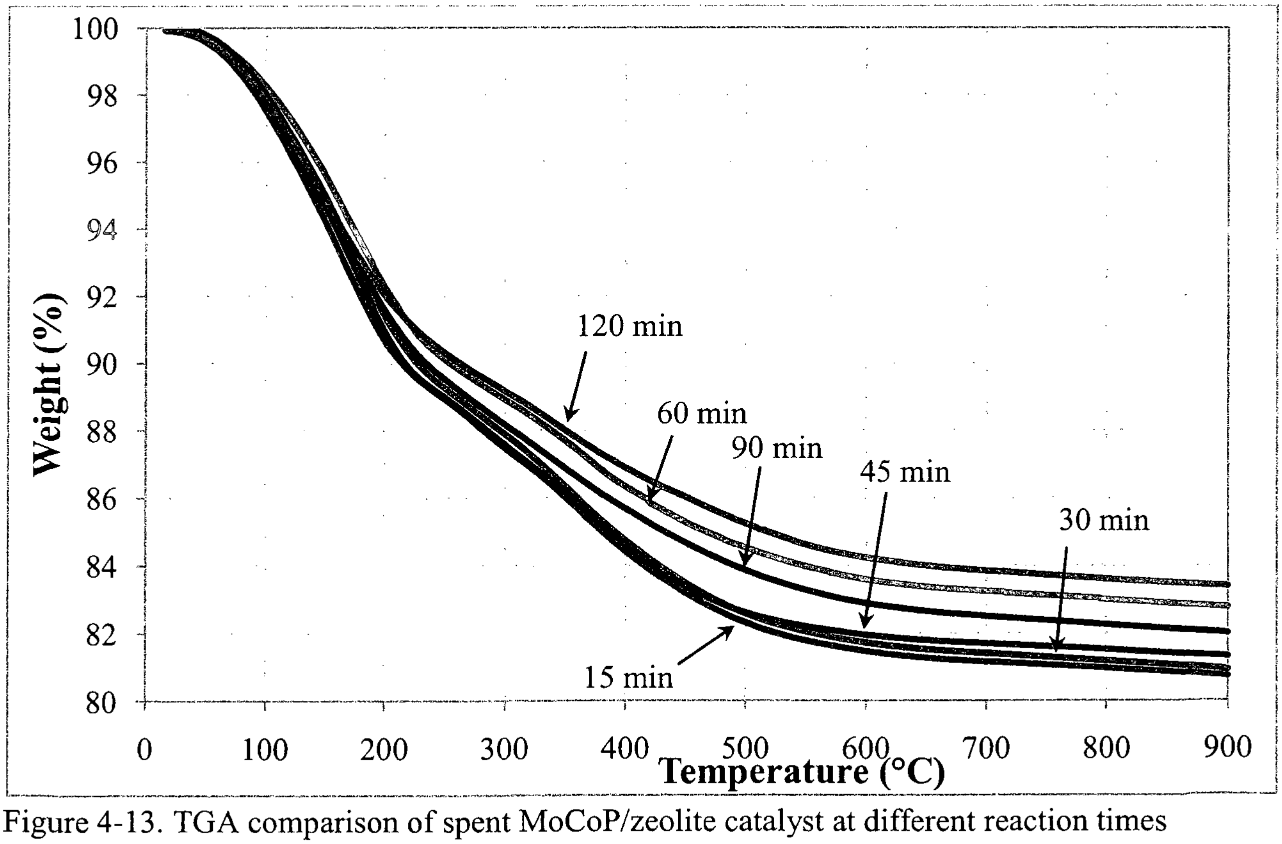


Figure 4-13. TGA comparison of spent MoCoP/zeolite catalyst at different reaction times

water present to produce CO and $H_2$ (water-gas shift reaction). This would explain the lower hydrogen consumption seen at 120 min in Figure 4-3.

The TGA curves in Figure 4-14 show the effects of dilution of the glycerol feedstock on the amount of char deposited on the spent catalysts. As can be seen, the amount of char deposited on the catalyst was lower for the glycerol feedstock with less dilution. This is likely due to the immiscibility of the reaction products in the water present. The presence of water increases the local concentration of reaction products in a separate phase and hence facilitates the product condensation into much heavier compounds which deposit on the catalyst surface.

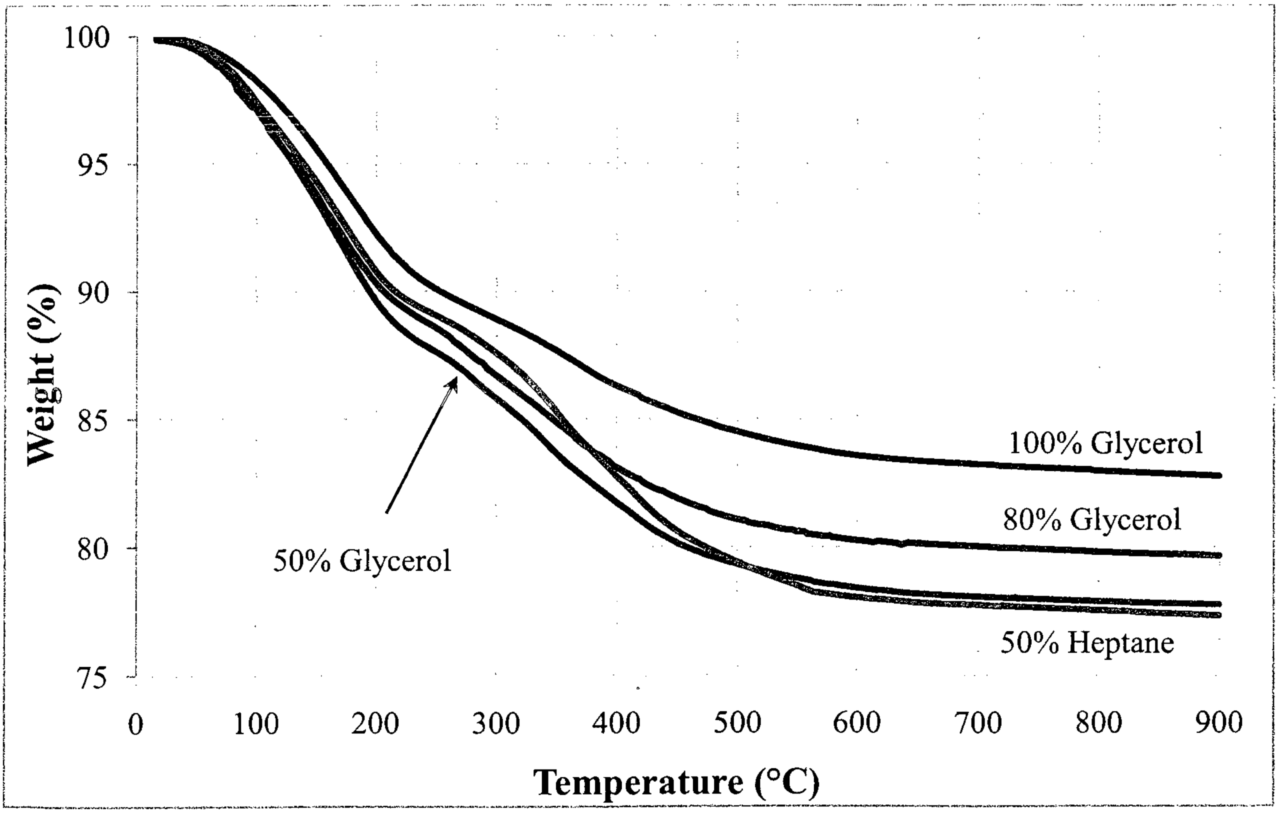


Figure 4-14. TGA comparison of spent MoCoP/zeolite catalyst after HDO of glycerol feedstock diluted with different amounts of water or heptane.

## 4.4 Conclusions

In this study, the optimum conditions for the hydrodeoxygenation of glycerol were investigated in the presence of MoCoP/zeolite catalyst. The conclusions may be summarized as follows:

(1) The HDO activity of the MoCoP/zeolite catalyst increased with extended reaction time up to 1 h.

(2) The activity of the MoCoP/zeolite catalyst for the bio-oil yield and glycerol conversion in HDO of glycerol exhibited maximum at around 300°C. Temperatures below 300°C were not effective in converting glycerol into bio-oil. Increased temperature was also found to decrease char yield and increase glycerol gasification.

(3) The initial pressure of hydrogen was found to greatly affect the HDO activity of CoMoP/zeolite catalyst. Bio-oil yield increased drastically with an increase in hydrogen pressure from 2.5 to 5 MPa..

(4) While dilution of the glycerol feedstock with water had a negative effect on bio-oil yield, HDO of pure glycerol produced the highest bio-oil yield (40 wt.% at 300°C, 1 h and 5 MPa $H_2$).

(5) The amount of char deposited on the spent catalyst decreased with increased reaction temperature and elevated initial hydrogen pressure.

## References

Boocock DG B, Mackay D, McPherson M, Nadeau S, Thurier R. *Can. J. Chem. Eng.* **57** (1979) 98-101.

Byambajav E, Ohtsuka Y. *Appl. Catal.* A **252** (2003) 193-204.

Czernik S, Maggi R, Peacocke GVC. CPL Press, UK (2002) 141-145.

Dasari, MA. et al. Low-pressure hydrogenolysis of glycerol to propylene glycol *Applied Catalysis A: General* **281** (2005) 225–231.

Elliott DC. *Energy Fuels* **21** (2007) 1792-1815.

EU Directive 2003/30/EC, The promotion of the use of biofuels and other renewable fuels for transport, 8 May 2003.

http://www.grace.com/engineeredmaterials/materialsciences/zeolites/ZeoliteStructure.aspx, retrieved July 6, 2010.

Lewis MJ, Kydd AR, Boorman MP, Van Rhyn HP. *Appl. Catal. A: Gen.* **84** (1992) 103.

Lopez RC, Lopez SG, Fierro GLJ, Lopez AA. *J. Catal.* **126** (1990) 8.

Marshall AT, Haverkamp RG. Production of hydrogen by the electrochemical reforming of glycerol–water solutions in a PEM electrolysis cell *Int. J. of Hydrogen Energy* **33** (2008) 4649-4654.

Okkerse C, Van Bekkum H. Fossil to green. *Green Chem.* **1** (1999) 107-114.

Radovic LR, Walker PL, Jenkins J. *Catal.* **82** (1983) 382-394.

Song C. Fuel processing for low-temperature and high-temperature fuel cells: challenges and opportunities for sustainable development in the 21st century. *Catal. Today* **77** (2002) 17-49.

Valliyappan, T. et al., Pyrolysis of glycerol for the production of hydrogen or syn gas. *Bioresour Technol.* **99** (2008) 4476–4483.

Yang Y, Gilbert A, Xu C Hydrodeoxygenation of bio-crude in supercritical hexane with sulfided CoMo and CoMoP catalysts supported on MgO: A model compound study using phenol, *Applied Catalysis A: General* **360** (2009) 242-249.

Yazdani, SS and Gonzalez, R, Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry *Current Opinion in Biotechnology* **18** (2007) 213–219.

Yokoyama S, Ogi T, Koguchi K, Nakamura E. *Liq. Fuels Technol.* **2** (1984) 115-163

Zhang, Y. et al., Inactivation of aldehyde dehydrogenase: A key factor for engineering 1,3-propanediol production by *Klebsiella pneumoniae. Metabolic Engineering* **8** (2006) 578–586.

# CHAPTER 5

## Conclusions and Recommended Future Work

### 5.1 Summary and Conclusions

This thesis conducted novel research into the conversion of glycerol into a higher caloric value bio-oil by simultaneous hydrodeoxygenation (high-pressure deoxygenation under a hydrogen atmosphere) and oligomerization reactions in the presence of a catalyst. Under optimum conditions of 300°C, 5 MPa initial hydrogen pressure, 100% glycerol feed, 1 h reaction time and oxidized MoCoP/zeolite catalyst, high yields of bio-oil (up to 40 wt.%) with a HHV of 33 MJ/kg were obtained. Two parts of work have been studied in this thesis: (1) Hydrodeoxygenation of Glycerol into Bio-crude - Catalyst Screening; (2) Hydrodeoxygenation of Glycerol into Bio-crude - Process Optimization. The detailed conclusions for each part of this work are summarized as follows.

#### Part-I: Hydrodeoxygenation of Glycerol into Bio-crude: Catalyst Screening

(1) Acid-supported catalysts are more effective for converting glycerol into bio-oil than either basic- or neutral-supported catalysts.

(2) Zeolite-supported MoCoP catalyst was found to be the most effective in the production of bio-oil from glycerol.

(3) Both reduction and sulfidation of the MoCoP/zeolite catalyst were found to have a marked negative effect on bio-oil yields.

(4) The presence of P in the catalyst reduced the amount of char deposited on the spent catalysts.

(5) GC/MS analysis revealed that the bio-oil produced by hydrodeoxygenation of glycerol is composed mainly of substituted phenols, ketones and to a lesser extent alcohols, ethers and cycloalkanes.

(6) The bio-oil produced has HHVs up to 33MJ/kg compared to the HHV of 16 MJ/kg for the glycerol feedstock indicating hydrodeoxygenation is a promising technique for the upgrading of glycerol into bio-oil/bio-crude with a significantly increased heating value.

## Part-II: Hydrodeoxygenation of Glycerol into Bio-crude: Process Optimization

(1) The HDO activity of the MoCoP/zeolite catalyst increased with extended reaction time up to 1 h.

(2) The activity of the MoCoP/zeolite catalyst for the bio-oil yield and glycerol conversion in HDO of glycerol exhibited maximum at around 300°C. Temperatures below 300°C were not effective in converting glycerol into bio-oil. Increased temperature was also found to decrease char yield and increase glycerol gasification.

(3) The initial pressure of hydrogen was found to greatly affect the HDO activity of CoMoP/zeolite catalyst. Bio-oil yield increased drastically with an increase in hydrogen pressure from 2.5 to 5 MPa.

(4) Dilution of the glycerol feedstock with water had a negative effect on bio-oil yield, while HDO of pure glycerol produced the highest bio-oil yield (40 wt.% at 300°C, 1 h and 5 MPa $H_2$).

(5) The amount of char deposited on the spent catalyst decreased with increased reaction temperature, and elevated initial hydrogen pressure.

## 5.2 Recommendations for Future Work

This thesis work involved bench-scale exploration tests in the hydrodeoxygenation of glycerol into bio-oil. Although the experiments results are very promising, more work is needed to scale-up the production of high quality bio-crude from bench-scale to pilot-scale or even industrial scale.

For bio-crude production through hydrodeoxygenation of glycerol, the following recommendations may be considered for future research:

(1) Based on the present experimental results and available literature, it is possible to produce higher yields of bio-oil by further optimizing the experimental parameters such as catalyst loading, different catalyst support materials and the use of co-solvents.

(2) The bio-oil produced in this research is not suitable for use as a transportation fuel directly. It is too viscous and contains appreciable oxygen. Further upgrading of the bio-oil is required in order to increase the hydrogen content and further decrease the oxygen content. More research is required to determine if this can be accomplished in a more effective one-step HDO process or requires a subsequent upgrading stage.

(3) The liquid product separation procedure for heavy oil recovery (presently by evaporation) may be improved by using more effective solvents for extraction (since ethyl acetate is slightly soluble in water).

(4) Instead of using HCl, $HNO_3$ or $H_3PO_4$ may be used to acidify the MoCoP/zeolite catalysts. This would eliminate the formation of metal chlorides and, in the case of $H_3PO_4$, pre-phosphorate the catalyst.

(5) Optimization of zeolite acidification may reduce or eliminate the apparent destruction of the zeolite crystal structure that was observed.

(6) Other types of support materials, such as Y-type zeolite, and catalyst metals, such as Pt, may be investigated.

(7) A more robust reactor capable of withstanding higher pressures would enable the investigation of glycerol HDO reactions at stoichiometric and greater-than-stoichiometric hydrogen pressures.

(8) The use of a continuous flow-type reactor in the HDO of glycerol should be investigated in future work, with especial care given to the problems of feed viscosity.

(9) The long-term catalytic effectiveness of the zeolite-supported MoCoP catalyst, or other, possibly more effective, catalyst combinations, should be examined with longer reaction times and also with the use of regenerated catalyst.

(10) The present work indicates that HDO of pure glycerol can be achieved. The feed streams from bio-diesel production will not be pure. Investigation of crude glycerol from a bio-diesel production facility would be of enormous benefit in determining if this process is feasible on an industrial scale.