Production of Bio-crude from Forestry Waste by Hydro-liquefaction in Sub-/Super-critical Methanol and Upgrading of Bio-crude by Hydro-treating

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Abstract

Bio-energy is renewable and clean (with trace amount of sulfur and neutral in terms of CO_2 emission), and abundant in resource, thus it could be a securable and sustainable energy for future. Due to the declining reserve of light crude oil, there is increased interest in producing bio-fuels (bio-ethanol, bio-diesel and bio-oils) from biomass resources. Bio-crude, produced from lignocellulosic biomass/wastes by high-pressure direct liquefaction, has been found more advantageous than conventional bio-oil generated by pyrolysis since a bio-crude normally contains a greater heating value than pyrolysis oil. Bio-crude has a potential to be upgraded into high quality fuel oils or transportation fuels by hydro-treatment.

As Part-I of this thesis work, hydro-liquefaction of a woody biomass (birch powder) in sub-/super-critical methanol without and with catalysts was investigated with an autoclave reactor at temperatures of 200-400°C and initial pressure of hydrogen varying from 2.0 to 10.0 MPa. The liquid products were separated into water soluble oil and heavy oil (as bio-crude) by extraction with water and acetone. Without catalyst, the yields of heavy oil and water soluble oil were in the ranges of 2.4-25.5 wt% and 1.2-17.0 wt%, respectively, depending strongly on reaction temperature, reaction time and initial pressure of hydrogen. The optimum temperature for the production of heavy oil and water soluble oil was found to be at around 350°C, while longer residence time and lower initial H_2 pressure were found to be favorite conditions for higher oil production. Addition of a basic catalyst, such as NaOH, K_2CO_3 and Rb_2CO_3, significantly promotes biomass conversion and increases yields of oily products in the treatments at temperatures less than 300°C. The yield of heavy oil is as high as 30 wt% for the liquefaction operation in the presence of 5 wt% Rb_2CO_3 at 300°C and 2 MPa of H_2 for 60 min. The heavy oil product consists of a high concentration of phenol derivatives, esters and benzene derivatives, and has higher carbon content, a much lower concentration of oxygen content, and a significantly increased heating value (> 30 MJ/kg) compared with the raw woody biomass.

In the Part-II of this research, hydrodeoxygenation (HDO) of bio-crude was investigated using phenol as the model compound in supercritical hexane at temperatures of 300-450°C and initial pressure of hydrogen 5.0 MPa with MgO-supported sulfided CoMo with and without phosphorus as the catalyst promoter. The oily products after hydro-treatment were characterized by GC/MS and FTIR. Both MgO-supported catalysts proved to be effective for hydrodeoxygenation of phenol leading to significantly increased yields of reduced hydrocarbon products, such as benzene and cyclohexyl-aromatics, at temperatures higher than 350°C, while CoMoP/MgO showed superior activity in HDO of phenol. In the presence of CoMoP/MgO for 60 min and at 450°C, the treatment of phenol yielded a product containing approximately 65 wt% benzene and >10 wt% cyclohexyl-compounds. The fresh and spent catalysts were thoroughly characterized by ICP-AES, N_2 isothermal adsorption, XRD, XPS and TGA, and the roles of the phosphorus as the catalyst promoter and the effects of MgO as a basic support were also discussed.

In the Part-III of this work, hydrodeoxygenation (HDO) of bio-crude derived from direct liquefaction of birch powder was investigated in supercritical hexane at temperatures of 300-380°C under hydrogen of cold pressure of 2.0-10.0 MPa with MgO-supported sulfided CoMo with phosphorus as the catalyst promoter. The oil products were characterized by GC-MS, elemental analysis and FT-IR, and the fresh and spent catalysts by ICP-AES, N_2 isothermal adsorption, XRD, XPS and TGA. The hydro-treatment at temperatures higher than 350°C with the CoMoP/MgO catalyst proved to be effective for de-oxygenating the bio-crude sample, leading to significantly reduced contents of phenolic compounds and carboxylic acids/esters and greatly increased concentrations of oxygen-lean/free compounds such as ketones and hydrocarbons in the hydro-treated oil products. From the elemental analysis results, the upgraded oil products contained higher concentrations of carbon and hydrogen, and much lower concentrations of oxygen and nitrogen, resulting in an increased caloric values. For instance, the treatment at 350°C for 60 min under 5 MPa H_2 produced an upgraded oil with 0.2 wt% N, 16.1 wt% O and 34 MJ/kg HHV, compared with 0.6 wt% N, 26.2 wt% O and 27.1 MJ/kg HHV for the raw bio-crude.

Keywords: Bio-crude; Hydro-liquefaction; Woody biomass; Hydrodeoxygenation; Hydro-treating; Sub-critical methanol; Super-critical methanol; CoMo/MgO; CoMoP/MgO; Sulfided catalysts, Supercritical hexane.

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CHAPTER 1

Introduction

1.1 Background

During the past century the world's energy demand was met heavily by fossil fuels, detailed as: 30% petroleum, 23% natural gas, 22% coal, 6% nuclear, and 19% renewable [1]. The era of fossil-resources-based energy and chemical industries is expected to phase out gradually in the course of the 21st century because of declining fossil resources [2]. Due to the increasing concerns over greenhouse gas emissions and energy security, there is a resurgence of interest in renewable bio-energy. Biomass feedstock such as agricultural/forestry residues and woodwastes (harvest residues, slash, sawdust, bark, etc.) can be an large source for energy, fuels, chemicals and materials [3,4]. Many countries have legislation in place to promote using biomass energy and bio-fuels. For example, the European Union has set an objective to substitute biomass-derived fuels (bio-fuels) for the conventional fuels in transport sector with a market share of 5.75% by the end of 2010 [5]. 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 US President in December 2007 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.

Bio-energy is all forms of renewable energy that are derived from biomass feedstocks. Biomass feedstock typically has a heating value of 8 MJ/kg for green matter and 17-23 MJ/kg for dry plant matter, which is comparable to that of low rank coal (lignite and sub-bituminous coals).

The earth's natural biomass replacement represents an energy supply of around 3000 EJ (3×10^{21} J) per year, or about 150 billion metric tons of dry biomass, about 6 times the world's total energy consumption. Although biomass resources are renewable, carbon-neutral, and remarkably massive in amount, they are very bulky and difficult to transport, handle, and store. Therefore, appropriate cost-effective technologies must be developed to convert them into liquid bio-fuels of a higher energy density and other valuable chemicals [6]. As summarized in Figure 1-1, biomass conversion technologies may be classified into two major categories: bio-chemical processes and thermo-chemical processes [7-9]. The biological technologies aim at recovering the sugars using acid/engineered enzymes to break down ligno-cellulosic materials, and hydrolyze the cellulose into glucose that will be fermented into ethanol. Development of new enzymes is still at the research stage, and most developed enzymes and the microorganisms are strongly dependent on chemical compositions of the feedstock, and therefore apply only to some specific homogenous feedstock. As such, the current fermentation-based technology does not make the cellulosic ethanol production economically viable. In addition, the use of fuel alcohols in place of gasoline requires modification of existing engines and delivery systems [10]. Thermo-chemical processes for the production of liquid bio-fuels include indirect liquefaction approaches gasification combined with various catalytic processes for production of synthetic fuels (e.g., methanol, ethanol and high quality diesel), and the direct liquefaction technologies (pyrolysis and high pressure liquefaction) for the production of bio-oil or bio-crude. The 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. Biomass direct liquefaction for the production of bio-oil/bio-crude has attracted increasing interest in recent years due to the skyrocketing crude oil price and the increasing concerns over greenhouse gas emissions. Bio-oil/bio-crude products can be upgraded and refined into high quality liquid fuels such as liquid transportation fuels [8].

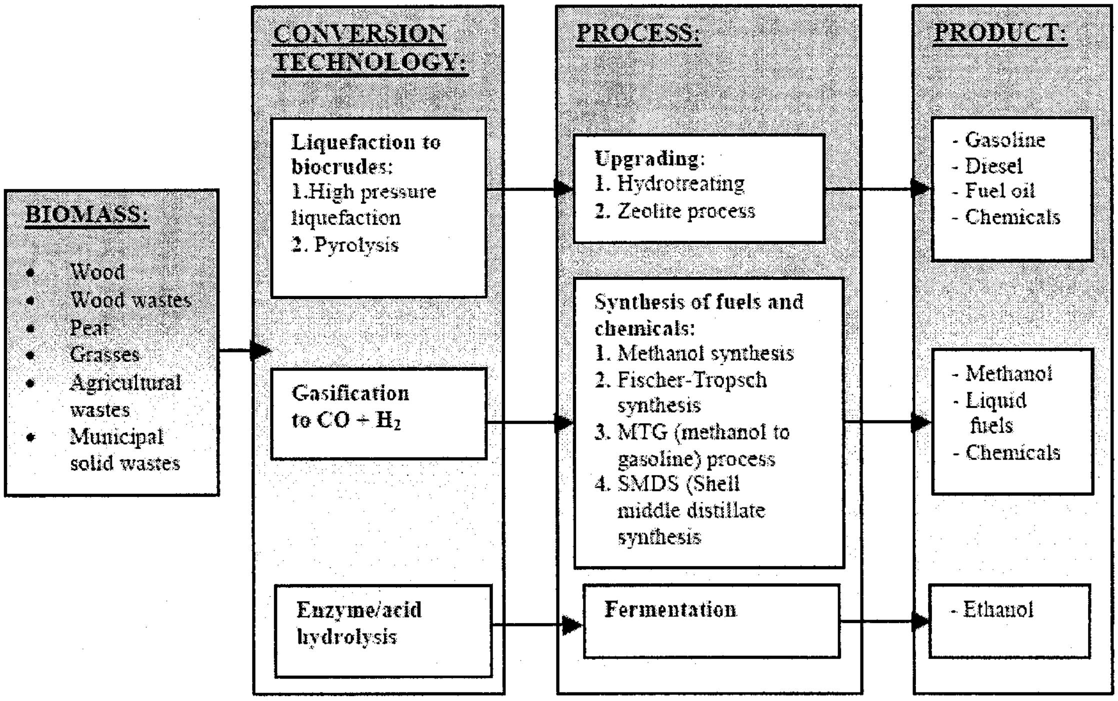

Figure 1-1 Routes from biomass to fuels and chemicals [7-9].

Fast pyrolysis (operating at a low pressure of 0.1-0.5 MPa but a high temperature > 500°C) is so far the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils have a high oxygen/water content and hence a lower caloric value (<20 MJ/kg, only about half of that of petroleum). Superior to the pyrolysis technology, high-pressure liquefaction technology with a suitable solvent (water or organics) and a catalyst, which normally operates at a moderate temperature <400°C but high pressure of 5-20 MPa, has the potential for producing liquid oils (also called bio-oils or bio-crudes) with much higher caloric values (25-35 MJ/kg) [6,11]. Hot-compressed or sub-/supercritical water treatment has been studied by many researchers for biomass liquefaction [12-16]. However, the drawbacks of using water as the solvent for liquefaction of coal or biomass include the following aspects: lower yields of the water-insoluble oil product (with a greater heating value) compared with those of water-soluble product (with a lower heating value), and higher oxygen content in the liquefied products, resulting in low liquid product heating values[17].

To enhance the yields of liquid oil products with reduced oxygen contents (hence a greater heating value), sub-/super-critical alcohols have been tested for liquefaction of ligno-cellulosic materials [11, 18-26]. Since these alcohols have critical temperatures and pressures lower than water, much moderate reaction conditions can be employed. Another advantages of using alcohols as the solvent for biomass liquefaction is that these 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 [6]. Among all the alcohols, ethanol and methanol have been widely used for biomass liquefaction. Miller et al. [27] studied the depolymerization of Kraft and organosolv-derived lignins in supercritical methanol or ethanol in the presence of KOH, when high conversions were realized, with only 7% ether insoluble material remaining after treating organosolv lignin in KOH/ethanol at 290°C. Cemek and Kucuk [26] reported the liquid yields of 44.4 wt% and 43.3 wt% in liquefaction of Verbascum stalk at 573 K with supercritical methanol and ethanol, respectively. The conversion was rapid, reaching the maximum value within 10–15 min. To enhance liquid yields further and to obtain liquid products with lower oxygen content, the supply of hydrogen during liquefaction has been proved to be effective [28]. In previous work by Xu et al.[11] hydro-liquefaction of a woody biomass (Jack pine powder) was studied in sub-/super-critical fluid of ethanol with and without iron-based catalysts (5 wt% FeS or $FeSO_4$), when a very high liquid yield at 63% was obtained in the operation at 623 K for 40 min with the presence of $FeSO_4$ and H_2 of initial pressure of 5.0 MPa. The research of high pressure direct liquefaction with alcohol solvents is still on a bench scale, so the cost of production is high, because of the construction cost of high pressure, high temperature reactor and use of organic solvents. However, the cost of production could be reduced with the recover and reuse of alcohol solvents in industry process.

Among all the supercritical organic solvents for biomass liquefaction, methanol appears to be the most promising with respect to its lower cost Minami and Saka [19, 20] have reported that 90% of beech wood was successfully decomposed in supercritical methanol, and the optimal conditions for the chemical conversion of woods in supercritical methanol were at 350°C/43MPa. Accordingly, **the primary objective** of the present research was to produce bio-crude from forestry waste streams (i.e., birch sawdust in this work) through high pressure direct liquefaction employing sub-/super-critical fluid of methanol at temperatures of 473-673K with and without catalyst under hydrogen atmosphere of initial pressure varying from 2.0 to 10.0 MPa.

Bio-oils/bio-crudes comprise of a complex mixture of oxygen-containing compounds in the form of phenol derivatives, benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols [11, 27, 29-32]. These compounds contribute to the oxygen content of the oil. In addition, water originating from both the moisture 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 [33,34]. The total oxygen content of bio-oils can be as high as 40-50 wt% for pyrolysis oils, and 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 different catalysts adopted [35,36]. The high oxygen content is a limitation for utilization of bio-oils as liquid transport fuels since their high oxygen contents cause high viscosity, low heating value, poor thermal and chemical stability, corrosivity (acidity) and immiscibility with hydrocarbon fuels [33,34,37]. Therefore, pyrolysis oils/bio-crudes must be upgraded by various means to reduce its oxygen content [36,38].

Two typical technologies for upgrading of bio-oils for fuel applications include catalytic cracking and catalytic hydro-treating. A catalytic cracking process, using cracking catalysts (zeolites, silica–alumina and molecular sieves), is performed at atmospheric pressure without hydrogen. The advantages of low-pressure operation without the need of hydrogen have attracted much interest in the literature on the upgrading of bio-oils [39–43]. The yield of hydrocarbons is however very low because of the high yields of char/coke and tar. Deposition of these undesired products on the catalyst would also cause serious problem of catalyst deactivation. As such, a periodical or continual regeneration of catalysts is necessary. In contrast, catalytic hydro-treating is operated under high pressure with hydrogen and/or in the presence of hydrogen donor solvents [44–46]. Over the past 20 years, significant efforts have been made in hydrodeoxygenation (HDO) of biomass-derived oils. Research efforts to study the catalytic chemistry and kinetics of hydrotreating various model compounds containing oxygen, such as phenolic compounds and aromatic ethers, have been recently reviewed by Furimsky [35] and Elliott [47]. Pacific Northwest National Laboratory (PNL/PNNL) employed a batch reactor to test hydro-treating of phenolic model compounds with various catalysts [48]. Commercial 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 most active. On the basis of other model compound studies involving o-cresol and naphthalene, Elliott, et al. concluded that NiMo with a phosphated alumina support was the most active for oxygen removal and hydrogen addition [49]. Addition a small amount of phosphorus in sulfided $NiMo/Al_2O_3$ catalyst has been shown to enhance both hydrodenitrogenation (HDN) and hydrodesulphurisation (HDS) activities, with less susceptibility to coke formation [50]. The addition of phosphorus to NiMo/Al_2O_3 leads to the formation of acid centers with intermediate strength. Zhang et al. [51] hydrotreated a pyrolysis oil using sulfided CoMoP/γ-Al_2O_3, where the reaction was operated in an autoclave filled with tetralin (a common hydrogen donor solvent) under the optimum conditions of 360°C and 2 MPa of cold hydrogen pressure. The oxygen content was reduced from 41.8 wt% for the crude oil to 3 wt% for the upgraded product.

Another key parameter determining the hydrodeoxygenation (HDO) activity of Mo, CoMo or NiMo catalysts is the type of support. The most common and conventional support is Al_2O_3, which has been widely used in hydro-treating catalysts on an industrial scale [52]. Extensive studies have been undertaken on CoMo and NiMo catalysts supported on alternative materials such as SiO_2, active carbon, TiO_2, ZrO_2, zeolites and various mixed oxides [53–57]. Centeno, et al. [58] compared the HDO abilities of 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 *para*-xylene medium. Initial 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 [58].

MgO as a basic support has attracted much less attention. Basic supports are however interesting for two main reasons as stated by Klicpera and Zdrazil [59]. First, the acid–base interaction between acidic MoO_3 and a basic support in the oxide precursors of the sulfided catalyst could promote dispersion of the Mo species in the catalyst. Second, the basic character of the support could inhibit coking which is rather intensive for conventional Al_2O_3-supported catalysts. The most active Co(Ni)Mo/MgO catalysts were found to be 1.5–2.3 times more active than their Al_2O_3-supported counterparts for the hydrodesulfurization of thiophene [60]. Although much research on applications of MgO-supported catalysts has been reported in literature [52, 61-63], the catalytic application of MgO supported catalysts to HDO of bio-oil is not available.

Therefore, **the second and the third objective** of the present work are to explore sulfided Co-Mo catalysts supported on MgO for bio-crude upgrading by hydrodeoxygenation (HDO), first using phenol as a model compound for bio-crude, and then the bio-crude obtained from direct liquefaction of birch wood. The hydro-treating operations were carried out in supercritical fluid hexane at temperatures of 350-450°C under 2-10 MPa hydrogen with sulfided MgO-supported Co-Mo with and without addition of phosphorus as the catalyst promoter.

In the present work, supercritical hexane was used as the solvent for the bio-crude hydro-treating operations. A supercritical fluid serves not only as a superb solvent to dissolve materials not normally soluble in either ambient liquid or vapour phase of the solvent, but as an excellent reaction medium of complete miscibility with the gas and liquid/vapor products from the processes, This provides a single-phase environment for reactions that would otherwise occur as a multiphase system under conventional conditions. An alkane (hexane, decane, dodecane, etc.) itself is not a hydrogen-donor, but in its supercritical state it is an excellent solvent for hydrogen gas, and when combined with a suitable catalyst it could act as an effective hydrogen donor through a so-called "hydrogen shuttling" mechanism [64,65]. Recently, supercritical hydrocarbon solvents such as decane, dodecane and hexadecane, paraffinic petroleum cuts, tetralin, decalin and toluene were used as effective hydro-treating reaction media for upgrading heavy oil or vacuum residua [64,65]. Hexane has a very low boiling point at 69°C and moderate critical temperature and pressure of 235 °C and 3.1 MPa, which makes it a potential reaction medium for hydro-treating of bio-oils. A unique advantage of employing a low boiling-point hydrocarbon solvent as the reaction medium lies in the fact that it can be easily separated and recycled from the upgraded products by distillation.

1.2 Research Objectives

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

(1) Produce high quality bio-crude from forestry waste streams (birch sawdust) by hydro-liquefaction in sub-/super-critical methanol, and determine the optimum liquefaction conditions (reaction temperature, reaction time, hydrogen pressure, solvent-to-biomass ratio and catalysts) for a greater yield of bio-crude;

(2) Using phenol as a model compound for bio-crude, hydro-deoxygenate the model compound in supercritical hexane at temperatures of 350-450°C under 2-10 MPa cold hydrogen pressure with sulfided Co-Mo catalysts supported on MgO, and examining the effects of addition of phosphorus (P) as a promoter to the catalyst.

(3) Employing the novel catalyst selected from (2), upgrade the bio-crude obtained from direct liquefaction of birch wood from (1) by hydro-de-oxygenation (HDO).

1.3 Organization of the Thesis

This thesis is composed of six chapters.

Chapter 1 – Introduction. It provides a general introduction and a brief literature review on the related fields of the present research work, describing the research background, state-of-the-art of the research and objectives of the present work.

Chapter 2 – Literature Review. It provides a detailed literature review on the related fields of the present research work, i.e, direct liquefaction of biomass for bio-crude, and upgrading bio-crude/model compounds by catalytic hydro-de-oxygenation.

Chapter 3 – Production of Bio-crude from Forestry Waste by Hydro-liquefaction in Sub-/Super-critical Methanol. It is a manuscript submitted to and accepted by *AIChE Journal* for publication (currently in press).

Chapter 4 – Hydrodeoxygenation of Bio-crude in Supercritical Hexane with Sulfided CoMo and CoMoP Catalysts Supported on MgO: A Model Compound Study Using Phenol. It is a manuscript submitted to *Journal of Applied Catalysis A: General* for publication (currently accepted).

Chapter 5 – Hydrodeoxygenation of Bio-crude in Supercritical Hexane with a Sulfided CoMoP Catalyst Supported on MgO. It is a manuscript submitted to *AIChE Journal* for publication (currently under view).

Chapter 6 – Conclusions. It presents the overall conclusions and recommendations for future work.

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CHAPTER 2

Literature Review on Direct Liquefaction of Biomass and Upgrading of Bio-oils

2.1 Introduction

Biomass direct liquefaction for the production of bio-oil/bio-crude has attracted increasing interest in recent years due to the skyrocketing crude oil price and the increasing concerns over greenhouse gas emissions. Pyrolysis and high pressure liquefaction are two main thermo-chemical technologies developed for direct liquefaction of biomass into bio-oil or bio-crude products. Fast pyrolysis (operating at a moderate pressure of 0.1-0.5 MPa but a high temperature > 500°C) is so far the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils consist of high oxygen/water contents and hence lower caloric value (<20 MJ/kg, only about half of that of petroleum). Superior to the pyrolysis technology, high-pressure liquefaction technology with a suitable solvent (water or organics) and catalyst, which normally operates at a moderate temperature (<400°C) but high pressure of 5-20 MPa, has the potential for producing 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 comprise of a complex mixture of oxygen-containing compounds in the form of phenol derivatives, benzene derivatives, hydroxyketones, carboxylic acids and esters, aldehydes and aliphatic and aromatic alcohols. These compounds contribute to high oxygen contents of the oils (as high as 30-50 wt%), which would result in not only a lower calorific value, but a high viscosity, poor thermal and chemical stability, corrosivity (acidity) and immiscibility with hydrocarbon fuels. To produce high-quality bio-oils for use as liquid transport fuels, pyrolysis oils/bio-crudes must be upgraded by various means to reduce its oxygen content. The objective of this review was to provide an overview of the advances in thermo-chemical direct liquefaction technologies for the production of bio-oils/bio-crudes from biomass, and the development of the upgrading technologies to produce high quality liquid transport fuels from bio-oils/bio-crudes.

2.2 Fast Pyrolysis Technology for Bio-oil Production

Thermochemical conversion of biomass into liquid fuels and valuable chemicals can be achieved by either pyrolysis or high-pressure liquefaction [1,2]. Pyrolysis of biomass is operated in an inert atmosphere at high temperature (400-800°C) at a low pressure (0.1-0.5 MPa) without catalyst. At a high temperature, solid lignocellulosic materials thermally decompose into fragments that would convert to oily compounds through homogeneous reactions in the gas phase, yielding about 50-75 % liquid products (pyrolysis oil or bio-oil). In contrast, high-pressure liquefaction is performed under an inert or preferable reducing atmosphere at a moderate temperature (<400°C) but high pressure (5-20 MPa). In a high-pressure liquefaction process, feedstock macro-molecule compounds are decomposed into fragments of light molecules in the presence of a suitable solvent (water, alcohol, alkanes, phenols, and tetralin, etc.) and a suitable catalyst. The biomass-derived fragments are unstable and reactive, would tend to repolymerize into oily compounds having various molecular weights [1].

Pyrolysis is a thermal degradation process in the absence of oxidizing atmosphere at 400-800°C, Heat is usually added indirectly in a variety of forms, although partial gasification and combustion may be employed to give direct heating. Gas, liquid, and char are produced, while their relative proportions depend very much on the pyrolysis parameters (heating rate and temperature). Fast or flash pyrolysis (with a high heating rate and short vapor residence time) is used to maximize liquid products [3]. Flash pyrolysis maximizes liquid yields at up to 75 wt % at a relatively low temperatures of typically 500°C but less than 650 °C, and at very high reaction rates of 1000 °C/s, or even 10000 °C/s, and short residence time of typically less than 1 s. Rapid heating and rapid quenching in a fast pyrolysis process produce intermediate liquid products, which condense to form liquid oil products before being further broken down into gaseous products. High heating rates also minimize char formation, and no char is formed under some conditions [4]. Flash pyrolysis at relatively high temperatures of above 700°C would lead to very high reaction rates and a very high gas formation up to 80 wt% [5].

Over the last two decades, fundamental research on fast or flash pyrolysis has shown that high yields of primary, non-equilibrium liquids and gases, including valuable chemicals or chemical intermediates and fuels, could be obtained from various biomass feedstocks including agricultural/forest residues and waste streams [6]. Fast pyrolysis oils (bio-oils from fast pyrolysis processes) are mixtures of multi-components derived from depolymerization and fragmentation of cellulose, hemi-cellulose and lignin [7-9]. Composition on typical properties of pyrolysis bio-oil and of a petroleum-based heavy fuel oil is shown in Table 2-1.

The 99.7% of bio-oil from fast pyrolysis, is a complex mixture composed of acids, alcohols, aldehydes, esters, ketones, sugars, guaiacols, syringols, furans, lignin derived phenols and extractible terpene with multi-functional groups [10]. Zhang et al. [11] separated the bio-oil into four fractions: aliphatic, aromatic, polar and non-volatile fragments by using solvent extraction and liquid chromatography on an aluminum column. Identification revealed high contents of acetic acids and hydroxyacetones present in the water (aqueous) phase, and more polar components and aromatic hydrocarbons in the oil phase. In general, fast pyrolysis bio-oils are a complex mixture, highly oxygenated with a great amount of large size molecules nearly involving all species of oxygenated organics, such as esters, ethers, aldehydes, ketones, phenols, carboxylic acids and alcohols [12].

Table 2-1. Typical properties of pyrolysis bio-oil and of a petroleum-based heavy fuel oil [9]

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. For example, the fast pyrolysis process employing circulating fluidized beds, originally developed by 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 fluidized bed is commercialized by Dynamotive Energy Systems Corp, which has a demonstration project in Ontario, Canada sited at Erie Flooring and Wood Products. However, pyrolysis oils consist of high oxygen/water contents and hence lower caloric value (<20 MJ/kg, only about half of that of petroleum), and they are strongly acidic and corrosive. As a result, pyrolysis oil is not regarded as an ideal liquid fuel for heat and power generation, and without upgrading it cannot be used as a liquid transport fuel. Bio-oil has a content of water as high as 15–30 wt% derived from the original moisture in the feedstock and the product of dehydration during the pyrolysis reaction and storage. The presence of water lowers the heating value and flame temperature in combustion [13]. The removing of water from pyrolysis oil is problematic, because bio-oil heating results in rapid polymerization and increased viscosity. The presence of high content of oxygen creates the primary issue for the differences between bio-oils and hydrocarbon fuels. The high oxygen content leads to the lower energy density than the conventional fossil fuel and the immiscibility with hydrocarbon fuels. Pyrolysis bio-oils comprise substantial amounts of carboxylic acids, such as acetic and formic acids, which leads to a pH values as low as 2–3 [14]. The strong acidity makes bio-oil very corrosive and extremely severe at elevated temperature, which imposes more requirements on the construction materials of the storage vessels, and further upgrading process before it can be used as a liquid transport fuel [7].

2.3 High-pressure Liquefaction Technology for Bio-crude Production

Compared with the fast pyrolysis technology, high-pressure liquefaction technology is a superior direct liquefaction technology, which produce higher quality bio-oil with better chemical and physical perporties. The high-pressure liquefaction technology also has the potential for producing heavy liquid oils or bio-crudes (with increased heating values) and a range of chemicals including vanillin, phenols, aldehydes, and acetic acids, etc. A pioneer work of high-pressure biomass direct liquefaction technology was reported by Appell et al. [15] at the

Pittsburgh Energy Technology Center (PETC), where a variety of lignocellulosic materials were efficiently converted to oily products in water at an elevated temperature in the presence of CO and Na_2CO_3 as the catalyst. The PETC's biomass direct liquefaction technology was further advanced by the research group led by Dr. D.C. Elliott at Pacific Northwest Laboratory in USA. In the 1980's, Elliot and co-workers have done excellent work on scaling up the pioneer work by Appell et al. and on utilizing the direct liquefaction oil products [16,17].

2.3.1 Biomass Liquefaction in Hot-compressed Solvents

High-pressure direct liquefaction processes normally operated at a moderate temperatures (200-450°C) but high pressure (>1 MPa) for longer residence time (10-60 min) in hot compressed water [18-22] or organic solvents such as anthracene oil [23,24], alcohols (methanol, ethanol, propanol and butanol) and acetone, etc [25-27]. Typical yields of liquid products for the high-pressure liquefaction processes were in the range of 20-60%. Although a high-pressure liquefaction process produces a lower yield of heavy oil (bio-crude), compared with a fast pyrolysis process (with a yield of bio-oil with a HHV of about 20 MJ/kg at 40-75%), the bio-crude products contain much higher caloric values (HHV= ~30 MJ/kg) [18, 22]. If comparing the gross energy yield (= yield×HHV), the two types of direct liquefaction processes are comparable. The yields of bio-crude depend on many operating parameters including temperature, pressure, residence time, type of solvents and 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 the biomass direct liquefaction processes to suppress the formation of char while enhancing the yield of liquid products [19]. There has been however very little research reported on the roles that a catalyst plays in the direct liquefaction process. Appell et al. proposed the following mechanism for sodium carbonate-catalyzed liquefaction of carbohydrate in the presence of carbon monoxide [28].

Reaction of sodium carbonate and water with carbon monoxide, to yield sodium formate:

$Na_2CO_3 + 2CO + H_2O \rightarrow 2HCOONa + CO_2$

Dehydration of vicinal hydroxyl groups in a carbohydrate to an enol, followed by isomerization to ketone:

$CH(OH)\text{-}CH(OH)\text{-} \rightarrow \text{-}CH{=}C(OH)\text{-} + H_2O \rightarrow \text{-}CH_2\text{-}CO\text{-} + H_2O$

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

$HCOO^- + \text{-}CH_2\text{-}CO\text{-} \rightarrow \text{-}CH_2\text{-}CH\text{-}(O^-)\text{-} + CO_2$

$\text{-}CH_2\text{-}CH\text{-}(O^-)\text{-} + H_2O \rightarrow \text{-}CH_2\text{-}CH\text{-}(OH)\text{-} + OH^-$

The hydroxyl ion reacts with additional carbon monoxide to regenerate the formate ion

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

According to this mechanism, deoxygenation occurs through decarboxylation from ester formed by the hydroxyl group and formate ion derived from the 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 [29]. The micellar-like broken down fragments produced by hydrolysis are then degraded to smaller compounds by dehydration, dehydrogenation, and decarboxylation.

Glycerine was used for direct liquefaction of beech wood with the presence of Na_2CO_3 or KOH as the catalyst [30]. The most important variables appear to be temperature, amount of alkali and the nominal reaction time. In the presence of Na_2CO_3, a very high total oil yield (68.4%) was obtained, while the solubility in gasoline of the as-produced high polarity oil 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, and the oil yields could be promoted significantly by the addition of an alkaline salt such as NaOH, Na_2CO_3, KOH and K_2CO_3. Qu et al. [18] carried out direct liquefaction of Chinese fir in water in an autoclave at 280–360°C and for 10–30 min, where the maximum heavy oil yield of 24 wt% was obtained at 320°C for 10 min reaction. While the effect of reaction temperature on the yield of heavy oil was found less significant in the range of 280–360°C, addition of catalyst and/or hydrogen as a stabilizer (for stabilizing the intermediate liquid products) was very effective for increasing the yields of heavy oils. Karagoz et al. [31] performed hydrothermal treatment of woody biomass at 280°C for 15 min in the presence of an alkaline solution (NaOH, Na_2CO_3, KOH and K_2CO_3). Based on the biomass conversion and the yields 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 but favors the formation of oil products. However, the activity of an alkaline catalyst appeared to depend on the properties and type of biomass feedstock. Zhong et al. [32] carried direct liquefaction of different various types of woody biomass in hot-compressed water at 280–360°C, and a heavy oil yield of 30% coupled with a residue yield of less than 10% was obtained for all the wood samples tested. However, their experimental results showed with a feedstock of lower lignin content, the addition of K_2CO_3 catalyst was less effective for the production of oil products, although the catalyst reduced the residue yield for all the woods tested.

Acids were not regarded as effective catalysts for the biomass high-pressure liquefaction process, except for the processes employing phenol. Zhang et al. [33] investigated liquefaction of wood powder of 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 85% phosphoric acid and 36% sulfuric acid were effective for enhancing the liquefaction (phenolysis) efficiencies. It was found that an extremely low yield (<5 wt%) of solid residue was obtained from the operation at 150°C for 2 h when phosphoric or sulfuric acid was used.

2.3.2 Biomass Liquefaction in Sub-/Supercritical Fluids

Recently, near-critical or supercritical fluids, compressed solvents above their critical temperatures/pressures, have been investigated for biomass direct liquefaction processes. A supercritical fluid has unique ability to dissolve materials not normally soluble in either liquid or vapour phase and has complete miscibility with the liquid/vapour products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions [34,35]. Sub-/super-critical water was used for biomass liquefaction in many studies [36-42]. Qian et al. [42] researched on liquefaction of woody biomass in water with an autoclave reactor operated at 280–420°C with sodium carbonate as the catalyst. The experimental results demonstrated that the maximum yield of heavy oil of 53.3% was obtained at around 380°C.

Although water is regarded as the most environmentally friendly solvent, a drawback of utilizing water as the biomass liquefaction solvent lies in the fact that the yield of water-insoluble oil product (with a greater heating value) was generally lower than that of aqueous (water-soluble) products, and the gas formation became significant in supercritical water [43,44]. To improve the yields of liquid oil products of a greater calorific value, sub-/supercritical alcohols have been widely tested for liquefaction of lignocellulosic materials [45-53]. Since these alcohols have critical temperatures and pressures lower than water, much moderate reaction conditions can be employed. Another advantage of using alcohols as the solvent for biomass liquefaction is that these 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 [54]. Among all the alcohols tested, ethanol and methanol have been more commonly employed. Miller et al. [27] studied the depolymerization of Kraft and organosolv-derived lignins in supercritical methanol or ethanol in the presence of KOH, when high biomass conversions were realized. The ether insoluble material remaining after treating an organosolv lignin ethanol at 290°C in the presence of KOH was as low as 7 wt%. Cemek and Kucuk [26] reported the liquid yields of 44.4 wt% and 43.3 wt% in liquefaction of Verbascum stalk at 300°C with supercritical methanol and ethanol, respectively. The conversion was rapid, reaching the maximum value within 10–15 min. Minami and Saka [46-48] reported that 90% of beech wood was successfully decomposed in supercritical methanol and the optimal conditions for the chemical conversion of woods in supercritical methanol were at 350°C/43MPa. To enhance liquid yields further and to obtain oil products of a lower oxygen content, supply of hydrogen during liquefaction proved to be effective [45,55]. In the work by Xu et al. [45] hydro-liquefaction of a woody biomass (Jack pine powder) was studied in sub-/supercritical ethanol without and with iron-based catalysts (5 wt% FeS or $FeSO_4$), when a very high liquid yield at 63% was obtained in the operation at 350°C for 40 min with the presence of $FeSO_4$ and H_2 of an cold pressure of 5.0 MPa. The mechanism concerning the high activity for $FeSO_4$ is yet to clarified.

2.4 Bio-oil/Bio-crude Upgrading Processes

Biomass-based oils are very different from crude oils from petroleum sources; the sulfur content of bio-crudes is negligible, while they are rich in oxygen-containing molecules (see Table 2-2) [56]. Bio-oils/bio-crudes comprise of a complex mixture of oxygen-containing compounds in the form of phenol derivatives, benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols [57-59]. These compounds contribute to the oxygen content of the oil. In addition, water originating from both the moisture 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 [60,61]. 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 the process conditions, e.g. temperature, residence time, heating rate and different catalysts adopted [62,63]. The high oxygen content is a limitation for utilization of bio-crude as liquid transport fuel since the high oxygen content of the oils causes high viscosity, poor thermal and chemical stability, corrosivity (acidity) and immiscibility with hydrocarbon fuels [60,61,64]. Therefore, the bio-crude products should be upgraded by reducing their oxygen content [63,65].

Technologies for upgrading of bio-oils for fuel applications include physical and chemical/catalytic approaches [7, 66]. 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 [66]. Although physically mixing a bio-oil with diesel directly aided by addition some surfactant may be the simplest way to use bio-oil as a liquid transport fuel, the accompanying corrosiveness to the engine and the subassemblies is inevitably serious.

Table 2-2 Elemental composition of bio-oil from wood and of heavy fuel oil [56].

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

Currently, two chemical approaches have been proposed and tested for upgrading of pyrolysis oils and bio-crudes from high-pressure direct liquefaction processes, analogous to the upgrading of heavy oils in a petroleum refinery, i.e., catalytic cracking and catalytic hydro-treating. A catalytic cracking process, using cracking catalysts (zeolites, silica–alumina and molecular sieves), is performed at atmospheric pressure without the requirement of 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 literature [67–71]. The yield of hydrocarbons is however very low because of the high yields of char/coke and tar. Deposition of these undesired products on the catalyst would also cause a serious problem of fast catalyst deactivation. As such, more frequent regeneration of catalysts is necessary.

In contrast, the other chemical method, i.e., catalytic hydrotreating is operated under high pressure with hydrogen and/or in the presence of hydrogen donor solvents [72–74]. Over the past 20 years, there have been wide-ranging efforts reported in the literature in the effort of the hydrodeoxygenation (HDO) of biomass-derived oils.

2.4.1 Hydro-treating of Model Compounds

Research efforts to study the catalytic chemistry and kinetics of hydrotreating 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) have been recently reviewed by Furimsky [62] and Elliott [75]. Pacific Northwest National Laboratory (PNL/PNNL) employed a batch reactor to test hydro-treating of phenolic model compounds with various catalysts [76]. Some key results are summarized as follows. Commercial 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 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. concluded that NiMo with a phosphated alumina support was the most active for oxygen removal and hydrogen addition [77], 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 small amounts of phosphorus in sulfided NiMo/Al_2O_3 catalyst resulted in positive effects on both hydrodenitrogenation (HDN) and hydrodesulphurisation (HDS) activities, with less susceptibility to coke formation [78]. Addition of phosphorus to NiMo/Al_2O_3 led to the formation of acid centers with intermediate strength. Due to the addition of phosphorus to NiMo/Al_2O_3, new Lewis and Brönsted acid sites on the catalyst surface were evidenced by FTIR analysis [79].

One of the key parameters determining the hydrodeoxygenation (HDO) activity of Mo, CoMo or NiMo catalysts is the type of support. 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 [80]. Extensive studies have been undertaken on CoMo and NiMo catalysts supported on alternative materials such as SiO_2, active carbon, TiO_2, ZrO_2, zeolites and various mixed oxides [81–85]. Centeno, et al. [86] 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 *para*-xylene medium. Initial studies showed that coke formation was an important cause for catalyst deactivation with the use of alumina support especially with compounds containing two oxygens such as guaiacols or catechols [86]. MgO as a basic support has attracted much less attention. Basic supports are however interesting for two main reasons as stated by Klicpera and Zdrazil [87]. First, the acid–base interaction between acidic MoO_3 and a basic support in the oxide precursors of the sulfided catalyst could promote dispersion of the Mo species in the catalyst. Second, the basic character of the support could inhibit coking which is rather intensive over the conventional Al_2O_3-supported catalysts. The most active Co(Ni)Mo/MgO catalysts were 1.5–2.3 times more active than their Al_2O_3-supported counterparts for the hydrodesulfurization of thiophene [88]. From the available literature however, no research has been reported on the effectiveness of MgO supported sulfided catalysts for HDO of bio-oils or model compounds.

2.4.2 Hydro-treating of Bio-oils

Extensive studies have mostly focused on using the conventional petroleum hydrotreating catalysts, i.e., sulfided CoMo and NiMo for hydro-treating of pyrolysis oils or bio-oils. Elloit et al. [89, 90] examined hydro-catalytic reactions of bio-oils obtained from a high-pressure liquefaction process with a continuous feed fixed bed reactor. Preliminary results showed that the sulfided form of the CoMo catalyst was much more active than the oxide form. The sulfided nickel catalyst exhibited similar activity as 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, containing about 15 wt.% O, was achieved with the sulphided CoMo/Al_2O_3 catalyst at 573 K [91]. Using the same bio-oil, Gevert et al. [92] 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 the catalyst with narrow pores. Elliott and co-workers [93-95] developed a two-step hydrotreating process for upgrading of pyrolysis oils. The first step involves a low temperature (270°C, 136 atm) catalytic treatment that hydrogenates the thermally unstable bio-oil compounds. The second step involves catalytic hydrogenation at higher temperature (400 °C, 136 atm). The same catalyst, i.e., a sulfided CoMo/Al_2O_3 or sulfided NiMo/Al_2O_3, was used for both steps. This process produced 40 wt% yields of the refined oil containing less than 1 wt % oxygen from the raw pyrolysis oils. Catalyst deactivation and gum formation in the lines were the major process challenges. Churin et al. [96,97] conducted upgrading experiments on pyrolysis oil produced from olive oil. The authors reported that sulfided NiMo or CoMo on alumina or silica-alumina supports worked better than supported noble metal catalysts as the noble metal catalysts would be readily deactivated by poisoning, sintering, and fouling. The use of hydrogen donor solvent (tetrahydronaphthalene or tetralin) could lead to a marked improvement of the quality of the hydro-treated products, and reduced catalyst deactivation by coke deposition. Rochaet al. [98] evaluated a two-stage process involving hydropyrolysis of cellulose in the first stage, followed by hydroprocessing of the primary products still in a vapor phase, in the second stage. In the two stages, the H_2 pressure varied between 0.5 and 10MPa, and a fixed bed of sulfdided $NiMo/Al_2O_3$ catalyst was placed above the hydropyrolysis zone. The O content of the liquids after the first and the second-stage processing was 19 wt% and 9 wt%, respectively. A pyrolytic lignin, extracted from softwood fast pyrolysis bio-oil, was catalytic hydro-treated by Piskorz et al [99], using sulfided CoMo pellet catalyst, producing a light organic oil with 0.46% oxygen content. Zhang et al. [100] separated the oil phase from a fast pyrolysis oil, and the oil phase was hydro-treated over sulfided CoMoP/ γ-Al_2O_3. The reaction was operated in an autoclave reactor filled with tetralin (as a hydrogen donor solvent) under the optimum conditions of 360°C and hydrogen of a cold pressure at 2 MPa. The oxygen content was reduced from 41.8% for the crude bio-oil to 3% for the upgraded light fraction.

Although sulphided CoMo and NiMo catalysts are traditionally used in petroleum and bio-oil hydro-treatment, application of other types of catalysts, such as solid acids, solid bases and precious metal catalysts, to HDO of bio-oil have also been considered. Upgrading of fast pyrolysis oil using solid acid ($40SiO_2/TiO_2$-SO_4^{2-}) and solid base ($30K_2CO_3/Al_2O_3$-NaOH) catalysts at 50°C for 5 h was investigated by Zhang et al. [101], in which the dynamic viscosity of the bio-oil was lowered markedly. The density of the upgraded bio-oil was reduced from 1.24 to 0.96 kg/m^3, and the gross calorific value increased from 16 MJ/kg for the original bio-oil to 24 MJ/kg for the upgrade bio-oil. The results of GC/MS analysis showed that the de-carboxylation reaction in the bio-oil was promoted by both solid acid and solid base catalysts. Elliott [102] performed tests using a softwood-derived bio-oil and a bagasse-derived bio-oil over a carbon-supported ruthenium catalyst. The softwood-derived oil appeared to be more readily hydrogenated than the bagasse-derived bio-oil. As reported by Gagnon and Kaliaguine [109], polymerization occurred during the upgrading of the bio-oil produced by vacuum pyrolysis. Polymerization was more evident during the subsequent upgrading in the presence of a $NiWO/Al_2O_3$ catalyst at 598 K and about 18 MPa H_2, although significant oxygen removal was achieved. Soltes et al. [90, 104] upgraded pyrolytic oils from pine, where 20 catalyst formulations were tested. On the basis of batch reactor test results at 400 °C for 1 h, the Pd catalyst supported on alumina was determined to be most useful with the highest liquid yield. The alumina supported Pt or Re catalyst produced higher gas yields, while Ru and Rh were found to be the most active for 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. Developing highly active and less expensive catalysts for HDO of bio-oils or bio-crudes will continue to be a great challenge for future study.

2.5 Summary

(1) Fast pyrolysis is so far the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils consist of high oxygen and water content, and hence lower caloric value. Superior to the pyrolysis technology, high-pressure liquefaction technology with a suitable solvent and catalyst, which normally operates at a moderate temperature <400°C but high pressure of 5-20 MPa, has the potential for producing liquid oils with much higher caloric values (25-35 MJ/kg).

(2) Hot-compressed or sub-/supercritical water treatment with alkaline catalysts has been widely employed for biomass liquefaction mainly due to the fact that water is the most environmentally benign and safer solvent and the process does not require pre-drying of the feedstock which will yield much better energy efficiency.

(3) Sub-/super-critical alcohols are advantageous media for high-pressure direct liquefaction of biomass because the operation can be performed under more moderate temperatures and pressures, and can produce bio-crudes of relatively high molecular weight, of greater calorific value, and at a higher yield, compared with the processes with hot-compressed water.

(4) Bio-oils/bio-crudes comprise of a complex mixture of oxygen-containing compounds in the form of phenol derivatives, benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols. The high oxygen content will limit the usefulness of bio-oils as liquid transport fuels since their high oxygen content can result in high viscosity, poor thermal and chemical stability, corrosivity (acidity) and immiscibility with hydrocarbon fuels. Pyrolysis oils/bio-crudes need to be upgraded by various means to reduce their oxygen content.

(5) Catalytic cracking and catalytic hydro-treating are two typical technologies for upgrading of bio-oils for fuel applications. A catalytic cracking process, using cracking catalysts (zeolites, silica–alumina and molecular sieves), is performed at atmospheric pressure without the requirement of hydrogen. In contrast, catalytic hydro-treating is operated under high pressure (2-20 MPa) with hydrogen and/or in the presence of hydrogen donor solvents.

(6) Commercial sulfided catalysts (Al_2O_3-supported CoMo, NiMo, NiW, Ni, Co, Pd, and CuCrO) were widely used for hydro-de-oxygenation (HDO) of bio-oils and model compounds. . Pd catalyst supported on alumina has been found to be more useful with the highest liquid yield

than the conventional Mo-based catalysts. Catalyst deactivation due to coke formation has been identified as the major issue with the conventional alumina-supported catalysts.

(7) MgO is worthy to be investigated as a basic support for the bio-oil hydro-treating catalysts due to its potential advantages in the following two aspects: First, the acid–base interaction between acidic MoO_3 and a basic support in the oxide precursors of the sulfided catalyst could promote dispersion of the Mo species in the catalyst. Second, the basic character of the support could inhibit coking compared to the strongly-coking conventional Al_2O_3-supported catalysts.

(8) Developing highly active and less expensive catalysts for HDO of bio-oils or bio-crudes will continue to be a great challenge for future study.

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CHAPTER 3

Production of Bio-crude from Forestry Waste by Hydro-liquefaction in Sub-/Super-critical Methanol*

Hydro-liquefaction of a woody biomass (birch powder) in sub-/super-critical methanol without and with catalysts was investigated with an autoclave reactor at temperatures of 473-673K and initial pressure of hydrogen varying from 2.0 to 10.0 MPa. The liquid products were separated into water soluble oil and heavy oil (as bio-crude) by extraction with water and acetone. Without catalyst, the yields of heavy oil and water soluble oil were in the ranges of 2.4-25.5 wt% and 1.2-17.0 wt%, respectively, depending strongly on reaction temperature, reaction time and initial pressure of hydrogen. The optimum temperature for the production of heavy oil and water soluble oil was found to be at around 623K, while longer residence time and a lower initial H_2 pressure were found to be favorite conditions for the oil production. Addition of a basic catalyst, such as NaOH, K_2CO_3 and Rb_2CO_3, could significantly promote biomass conversion and increase yields of oily products in the treatments at temperatures less than 573K. The yield of heavy oil attained about 30 wt% for the liquefaction operation in the presence of 5 wt% Rb_2CO_3 at 573K and 2 MPa of H_2 for 60 min. The obtained heavy oil products consisted of a high concentration of phenol derivatives, esters and benzene derivatives, and they also contained a higher concentration of carbon, a much lower concentration of oxygen and a significantly increased heating value (> 30 MJ/kg) compared with the raw woody biomass.

Keywords: *bio-crude, hydro-liquefaction, woody biomass, sub-critical methanol, supercritical methanol, catalysts*

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3.1 Introduction

In the last century, the world has been heavily relying on fossil fuels for energy and chemical production, while the fossil resources are declining. Moreover, there is an increasing concerns over the environmental issues (such as greenhouse gas emission and global warming) associated with the use of fossil fuels. It is thus of strategically significance to explore alternatives to fossil resources for both energy and chemical production. Among all the potential alternatives to fossil resources, biomass such as wood, woodwaste (sawdust and woodfibre-based sludge from pulp/paper mills), forestry residues (limbs, bark, tree tops), energy crops and agricultural residues (wheat/rice straws and corn waste) can be a promising one since not only it represents an immense energy source (the global annual biomass production is about 6-8 times that the world energy consumption) but it is renewable[1,2]. Although biomass resources are renewable, carbon-neutral, and remarkably massive in amount, they are very bulky and difficult to transport, handle, and store. Therefore, appropriate biomass conversion technologies are required to convert them into gas, liquid fuels or other valuable chemicals. Biomass conversion technologies may be classified into two major categories: bio-chemical processes and thermo-chemical processes. Typical bio-chemical processes are anaerobic digestion of organic materials for production of biogas, and fermentation of sugar and starch crops and lignocellulosic materials to produce ethanol. Key thermo-chemical processes include direct combustion or co-firing (with coal), gasification combined with gas turbines for power generation, or gasification combined with various catalytic processes for production of synthetic fuels (e.g., methanol and high quality diesel), pyrolysis and direct liquefaction processes for production of bio-oil or bio-crude. Fast pyrolysis is so far the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils consist of high oxygen/water contents and hence lower caloric value (20-25 MJ/kg, only about half of that of petroleum), and they are strongly acidic and corrosive. Superior to the pyrolysis technology (operating at a mild pressure of 0.1-0.5 MPa but a high temperature > 500°C), direct liquefaction technology with a suitable solvent (water or organics) and catalyst, which is normally operating at <400°C but a high pressure of 5-20 MPa, has the potential for producing liquid oils (also called bio-crude) with much higher caloric values[3,4]. After further treatment and upgrading, the obtained bio-crude can be a potential substitute for petroleum for the production of fuels and a range of chemicals such as phenols, aldehydes, and organic acids, etc.

Supercritical fluids have found applications for the chemical conversion of lignocellulosic materials due to their unique properties, e.g., they possess unique transport properties (gas-like diffusivity and liquid-like density) and have complete miscibility with the liquid/vapor products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions[5]. In particular, supercritical fluids have the ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and hence to promote the gasification/liquefaction reactions[4]. Supercritical water treatment has been studied by many researchers for biomass liquefaction[6-10]. However, the drawbacks of utilizing water as the solvent for liquefaction of coal or biomass include the following aspects: lower yields of the water-insoluble oil product (with a greater heating value) compared with those of water-soluble product (with a lower heating value), and higher oxygen content in the liquefied products, resulting in low heating values for the liquid products[11].

To enhance the yields of liquid oil products with reduced oxygen contents (hence a greater heating value), sub-/super-critical alcohols have been tested for liquefaction of lignocellulosic materials[4,12-20]. Since these alcohols have critical temperatures and pressures lower than water, much milder reaction conditions can be employed. Another advantages of using alcohols as the solvent for biomass liquefaction is that these alcohols were 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[3]. Among all the alcohols, ethanol and methanol have been widely used for biomass liquefaction. Miller et al.[21] studied the depolymerization of Kraft and organosolv-derived lignins in supercritical methanol or ethanol in the presence of KOH, when high conversions were realized, with only 7% ether insoluble material remaining after treating organosolv lignin in KOH/ethanol at 290°C. Cemek and Kucuk[20] reported the liquid yields of 44.4 wt% and 43.3 wt% in liquefaction of Verbascum stalk at 573 K with supercritical methanol and ethanol, respectively. The conversion was rapid, reaching the maximum value within 10–15 min. To enhance liquid yields further and to obtain liquid products with lower oxygen contents, supply of hydrogen during liquefaction has been proved to be effective[22]. In a previous work by Xu et al.[4] hydro-liquefaction of a woody biomass (Jack pine powder) was studied in sub-/super-critical fluid of ethanol without and with iron-based catalysts (5 wt% FeS or $FeSO_4$), when a very high liquid yield at 63% was obtained in the operation at 623 K for 40 min with the presence of $FeSO_4$ and H_2 of initial pressure of 5.0 MPa.

Among all the supercritical organic solvents for biomass liquefaction, methanol appears to be more promising with respect to its lower cost compared with other alcohols or other organic solvents. Besides, methanol can be synthesized from hydrogen and carbon monoxide derived from biomass, thus it can be a renewable solvent just like ethanol. Minami et al.[12] investigated decomposition of lignin in supercritical methanol and indicated that the condensed linkages of lignin (e.g., 5-5 and β-1 linkages) were stable during the treatment with supercritical methanol, whereas the β-ether and α-ether linkages were rapidly cleaved. Minami and Saka[13,14] have reported that 90% of beech wood was successfully decomposed in supercritical methanol and the optimal conditions for the chemical conversion of woods in supercritical methanol were at 350°C/43MPa. In the present work, birch powder was liquefied in sub-/super-critical fluid of methanol at temperatures of 473-673K with and without catalyst under hydrogen atmosphere of initial pressure varying from 2.0 to 10.0 MPa.

3.2 Experimental

3.2.1 Materials

The birch wood (as a hardwood) sample used in this study was obtained from a local lumber mill (Northern Wood Ltd). After undergoing size-reduction by a chipper, the lumber was ground with a Wiley mill and screened. Particles smaller than 20 mesh (~ 0.8 mm) were used for the experiments. The wood powder was dried in an oven at 105°C in air for 24 hours before use. The proximate and ultimate analysis results of the birch sample and the chemical compositions of the ash from the wood sample are given in Table 3-1.

Table 3-1. Proximate and ultimate analyses of the birch wood sample and its mineral elemental compositions

Proximate analysis, wt% (d.b.(1))			Ultimate analysis, wt% (d.b.(1))				
VM	FC	Ash	C	H	N	S	O(2)
78.5	21.0	0.50	46.9	6.0	0.1	0.1	46.4

Major mineral elements in the sample, ppmw (d.b.)(3)								
Na	K	Mg	Ca	Mn	Fe	Zn	Al	Si
18	429	307	1585	131	37	39	19	5

[1] On a dry basis; [2] By difference; [3] Determined by ICP-AES

3.2.2 Hydro-liquefaction

The liquefaction experiments were conducted with a stainless steel autoclave. The stainless steel autoclave (Parr Instrument Company, model 4740; Heater model: 4921) had an effective volume of 75 ml with a pressure vessel of 1 inch I.D. and 5.6 inches inside depth. The birch powder, the catalyst (if needed), and the methanol solvent were weighed into the reactor in sequence. In a typical run, 4g of the dried woody biomass sample was weighed into the reactor, followed by adding catalyst (if required) in an amount of 5 wt% (w/w) of the woody biomass sample, and then 20g reagent-grade methanol was added. The catalysts used in this work were NaOH, K_2CO_3 and Rb_2CO_3. The air inside the reactor was displaced with ultrahigh purity hydrogen by repetitive operation of vacuuming and H_2-charging. Then, the reactor was sealed and pressurized to the pre-determined hydrogen pressure (between 2.0 and 10 MPa). The autoclave was heated at about 10 °C/min by an external electric heater to the desired temperature. As soon as the desired temperature was reached, the reactor was maintained at the temperature for a specified length of time for reaction. During the reaction, the pressure of the reactor was recorded in an interval of 10 min. After the desired reaction time had elapsed, the electric heater was removed from the reactor, and the reactor was cooled down to ambient temperature quickly with an electric fan and a wet cloth towel. Two to three duplicate runs were conducted for most of the experimental conditions and the relative errors for the liquefaction yields between the runs under the same conditions were ensured within 5% of the reported value of yields.

3.2.3 Separation of reaction products

Once the reactor was cooled to room temperature, the gas inside was collected in a gas cylinder, and was analyzed by GC-TCD. The total amount of gaseous product including CO. CO_2, $C_1 - C_3$ hydrocarbon species was denoted as "Gas" hereafter. The solid/liquid products were rinsed completely from the reactor with reagent-grade acetone. The resulted suspension was filtered under vacuum through a pre-weighed Whatman No.5 filter paper to recover the solid products (methanol and acetone insoluble). The recovered solids with the filter paper were dried for at least two hour in the oven at 105°C before weighing. The filtrate was evaporated under reduced pressure at 50°C to remove the solvents (acetone, methanol). After completely removing the solvents, the mixture of heavy oil (denoted as "HO" hereafter), water soluble oil (denoted as "WSO" hereafter) and pyrolytic water formed in the hydro-liquefaction process were weighed. This was followed by the addition of 50 ml of distilled water. The resulting mixture was sonicated for 40 minutes to allow the WSO dissolve into the water phase completely. After sonication, the resulted suspension was filtered to separate the water phase containing water soluble oil from heavy oil (retained by the filter paper). The obtained water-soluble oil solution was evaporated under reduced pressure at 80-90°C to remove water. It should however be noted that the method adopted in this work for the separation and quantification of the water soluble organic products would yield some errors due to the loss in the fraction of low boiling-point organics during the evaporation process. As a matter of fact, the efficient separation of water from water soluble organic compounds is a challenge due to the relatively high boiling point for water. Evaporating water under reduced pressure is so far the most widely adopted method by many researchers for quantifying the yields of the water soluble organic products. As such, the products of pyrolytic water and light ends (with low boiling points) were unrecoverable due to the loss in the evaporation process. The HO retained on the filter paper was rinsed with acetone to collect in an evaporation flask, and then was evaporated under reduced pressure at 50°C to completely remove acetone. The resulted WSO and HO were weighed, and then recovered to sample vials with 10 ml regent-grade acetone. In this work, the yields of Gas, WSO, HO and Char products were calculated to the dry organic matters (i.e., on a dry and ash/catalyst-free basis). There is a challenge in quantifying the yield of Char on a dry and ash/catalyst-free basis due to that fact that different catalyst compounds added have different solubility in the solvents. The recovered solid residue might consist of coke/char, ash and catalyst (if added) depending on the solubility of the catalyst compound in methanol/acetone solvents. For simplification, we assumed all the catalyst compounds were retained in the solid residues, and hence the Char yields were corrected by excluding the catalyst amount and the ash from the weight of the solid residues after drying. Although the above simplification would inevitably lead to some errors because there was a partition of the catalyst compound in the solid residue and the solvents/liquid products, the overall influence on the product yield calculation shall be minimum since the addition of each catalyst was only in an amount of 5 wt% (w/w) of the woody biomass sample. In addition, the extent of biomass conversion during the treatment was evaluated by "biomass conversion", a conversion based on the disappearance of the dry organic matter of the biomass solids.

3.2.4 Characterization

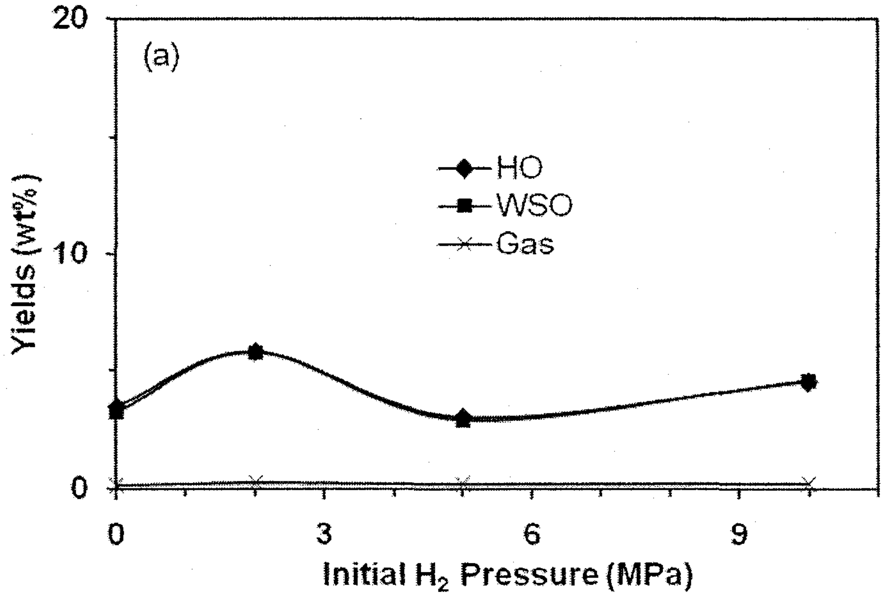
The compositions of gaseous products were determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. The elemental compositions (C, H and N) of Char, and HO and WSO were determined with a CEC (SCP) 240-XA elemental analyzer. The composition of oxygen (O) was estimated by difference, assuming negligible content of sulfur (S) in the products. The HO products were also analyzed by a gas chromatograph equipped with a mass selective detector [Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC equipped with VF-5 ms column (5% phenyl 95% dimethylpolysiloxane, 30 m×0.25 mm×0.25 μm); temperature program: 40°C (hold 2 min) →190°C (12°C/min) → 290°C (8 °C/min, hold 20 min)]. Compounds in heavy oil were identified by means of the NIST 98 MS library with the 2002 update. Non-thermal chromatographic techniques such as HPLC may be used to characterize the WSO products in future work. To examine the evolution of the crystalline forms in the wood samples and the dispersion states of the catalyst components (if added), X-ray diffraction (XRD) measurements were carried out by using Ni-filtered Cu-Kα radiation with a Philips PW 1050-3710 Diffractometer.

3.3 Results and Discussion

3.3.1 Influence of initial H_2 pressure

Figure 3-1 shows the product yields for the treatment at 200°C and 300°C for a fixed length of reaction time (30 min), while the initial pressure of H_2 was varied at different levels, i.e., 0.0MPa, 2.0MPa, 5.0 MPa and 10.0 MPa. It shall be noted that in the tests of 0.0 MPa H_2, the reactor was pressurized with 2.0 MPa ultra-pure N_2 (instead of H_2) to avoid boiling of the reactor content during the heating-up process. Since the critical temperature is 239°C for the methanol solvent, the liquefaction operations at 200 and 300°C represent the sub-critical and super-critical conditions, respectively. It is clearly shown in the Figure that at 300°C as the initial pressure of H_2 increased from 0.0 MPa to 2.0 MPa, both WSO and HO yields increased sharply. However, while the initial pressure of H_2 increased further from 2.0MPa to 10.0 MPa, both WSO and HO yields leveled off with slightly decreased values. In general, with the presence of H_2 in the liquefaction system, hydro-cracking reactions may occur to help break down the long chains of cellulose, hemi-cellulose and lignin (by cleavage of the aryl ether linkages in lignin[23]), forming intermediates which are the precursors for the liquid products. The cellulose/hemi-cellulose-derived intermediates may be stabilized by H_2 or hydrogen free radical

($H^{\bullet}$) to yield WSO products (carbohydrates, carboxylic acids and aldehydes), while the lignin-derived intermediates, mostly the aromatic free radicals ($Ar^{\bullet}$), may be stabilized rapidly by H_2 or hydrogen free radical ($H^{\bullet}$) to form HO products[24]. With a higher initial pressure of H_2 in the reaction system, generally higher yields of the liquid oil products may be expected, as observed in a previous study by Xu and Etcheverry[4], which is consistent with observation in this work as the initial pressure of H_2 increased from 0.0 MPa to 2.0 MPa. However, while the initial pressure of H_2 increased further to above 2.0 MPa, slightly different results were observed in this study as shown in Figure 3-1, where both WSO and HO yields leveled off at the initial pressure of H_2 of above 2 MPa. This difference may be attributed to different reactors used in reactions. For the work of Xu and Etcheverry, a fast-heated micro-reactor with an effective volume of 14 ml was used, while in the present study, an autoclave reactor with an effective volume of 75ml was employed. The micro-reactor was heated in fluidized sand bath, which could reach the specified temperature in very short time. While the autoclave was heated to the desired temperature (200-400°C) at the rate of approximately 10 °C/min, which means 20-40 minutes to reach the reaction temperature. The reported time commenced from the point when the desired temperature was reached, which means the actual residence time for the biomass was longer in the autoclave reactor that in the micro-reactor for a same reported reaction time. The difference in heating rates between these two types of reactors could result in different oil yields and compositions at the same reaction conditions (temperature and time, hydrogen pressure, etc.). Another big difference between the two types of reactors lies in the fact that the micro-reactor was supported on a mechanical shaker (set at 100 rpm), while the autoclave in present study was non-stirred. Compared with the well-shaken and fast-heated micro-reactor, the non-stirred autoclave reactor used in this work was operated under relatively less favourable heat and mass transfer conditions, leading to a lower hydrogen diffusion efficiency in the reaction medium in this work, which would hence explain the liquefaction efficiencies leveled off at the initial pressure of H_2 of above 2 MPa. Another possible explanation for the experimental results as shown in Figure 3-1, i.e., both WSO and HO yields decreased slightly with increasing H_2 pressure, might be that a higher H_2 pressure would enhance the hydro-de-oxygenation reaction (to form water) of the oil products in supercritical methanol, which would lead to reduced yields of oil products[25]. As the main objective of the present study was to produce bio-crude (heavy oil) from woodwaste, the remaining liquefaction operations were all carried out in H_2 of initial pressure of 2.0 MPa.



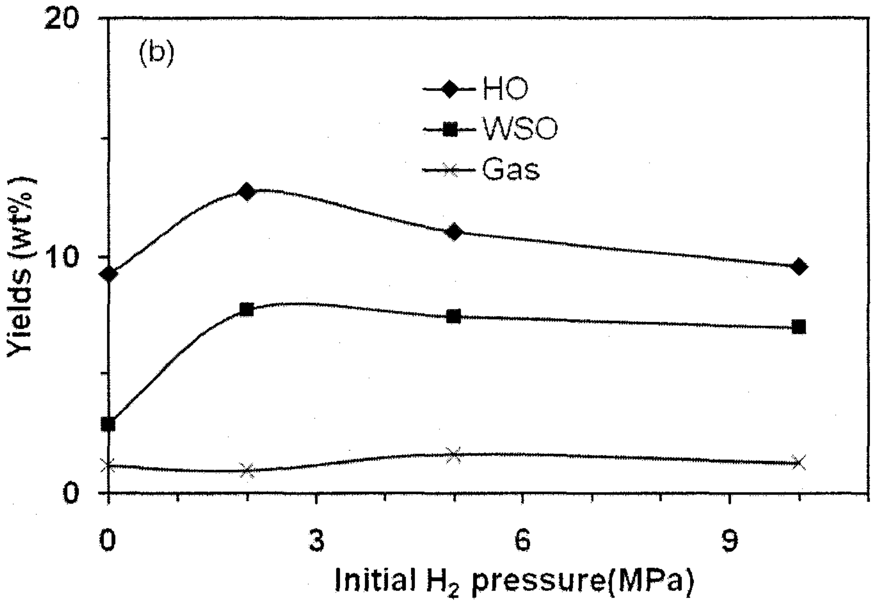


Figure 3-1. Yields of products as function of initial H_2 pressure in hydro-liquefaction of birch powder in methanol at 200°C (a) and 300°C (b). Other reaction conditions: Without catalyst; Reaction time of 30min; Solvent-to-Biomass ratio of 5.

3.3.2 Influence of residence time

Figure 3-2 shows the yields of liquefaction products at 200°C and 300°C for different lengths of reaction time ranging from 10 min to 480 min. As clearly shown in the Figure, the WSO, HO and Gas yields as well as the biomass conversion (revealed by the char yield) for both temperatures all follow the similar trend: increasing almost monotonically with reaction time. For instance, with supercritical methanol at 300°C, the biomass conversion climbed from 25% for 10 min to 40% for 60 min, and to 82% for 480 min. In the meanwhile, the WSO and HO yields increased from 3% and 10% % for 10 min, to 6% and 18% for 60 min, and to 18% and 26% for 480 min, respectively. As such, it may be concluded that longer residence time is a favorable condition for producing liquid oils (WSO and HO) from biomass in sub-/super-critical methanol, which is consistent with an earlier work by the authors' group on liquefaction of softwood biomass in supercritical ethanol[4]. The above observations however differ from some previous work on liquefaction of biomass in hot-compressed or sub-/super-critical water[26,27], where a declining HO yield and a climbing char yield was observed with increasing residence time due to condensation of the heavy oil products to form char/coke by condensation and dehydration reactions. The above comparison between alcohols and water may suggest that sub-/super-critical alcohols could be a more advantageous solvent over hot-compressed water for biomass liquefaction due to their superior performance in preventing condensation of the heavy oil products to form coke/char. The above superior performance of an alcohol solvent to water is likely due to the fact that supercritical alcohol can readily dissolve the liquid intermediates/products derived from cellulose, hemicelluloses, and lignin, leading to reduced concentrations of these unstable compounds, and hence retard their condensation and dehydration reactions.

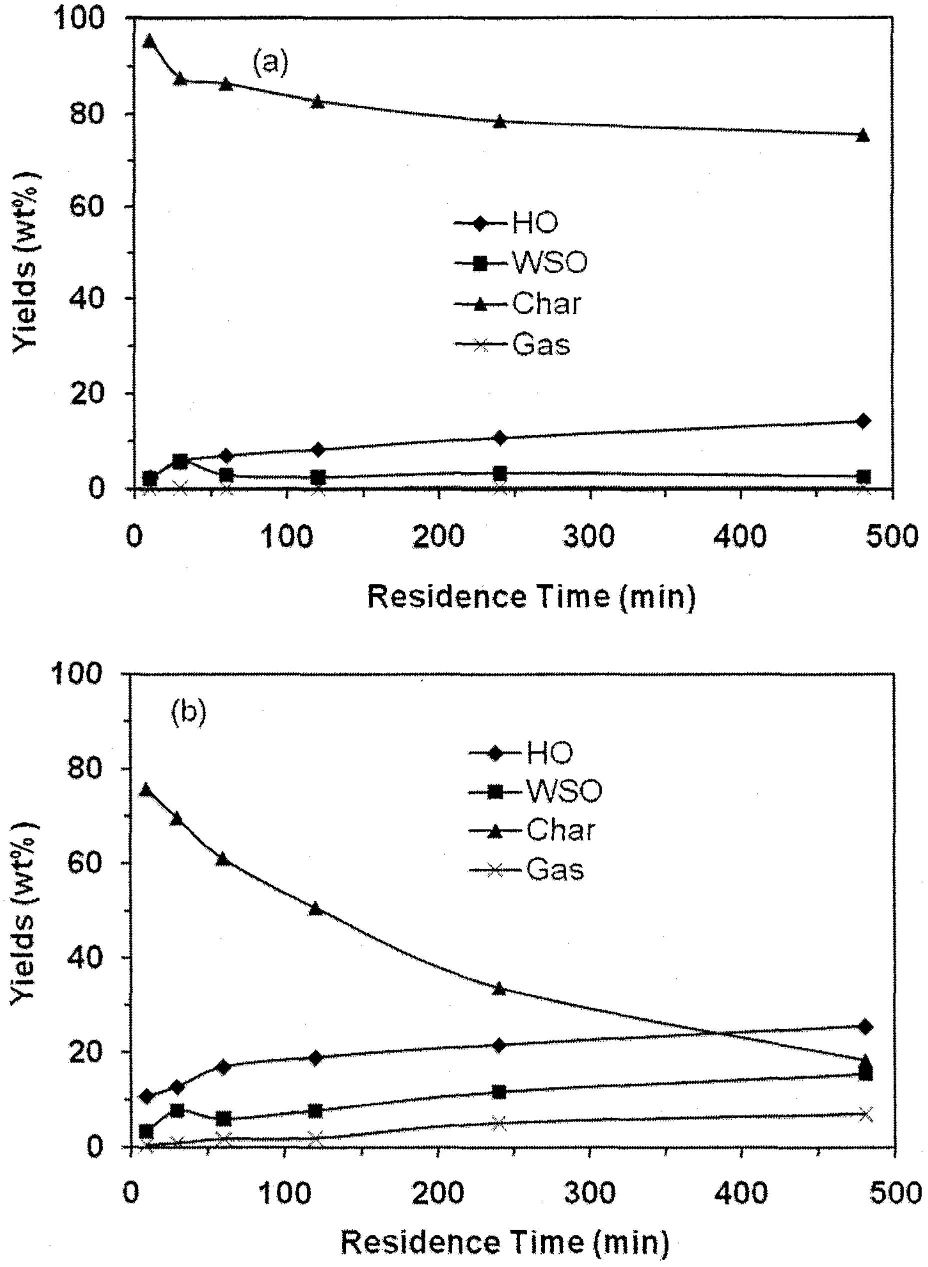


Figure 3-2. Yields of products as function of residence time in hydro-liquefaction of birch powder in methanol at 200°C (a) and 300°C (b). Other reaction conditions: Without catalyst; Initial H_2 pressure of 2MPa; Solvent-to-Biomass ratio of 5.

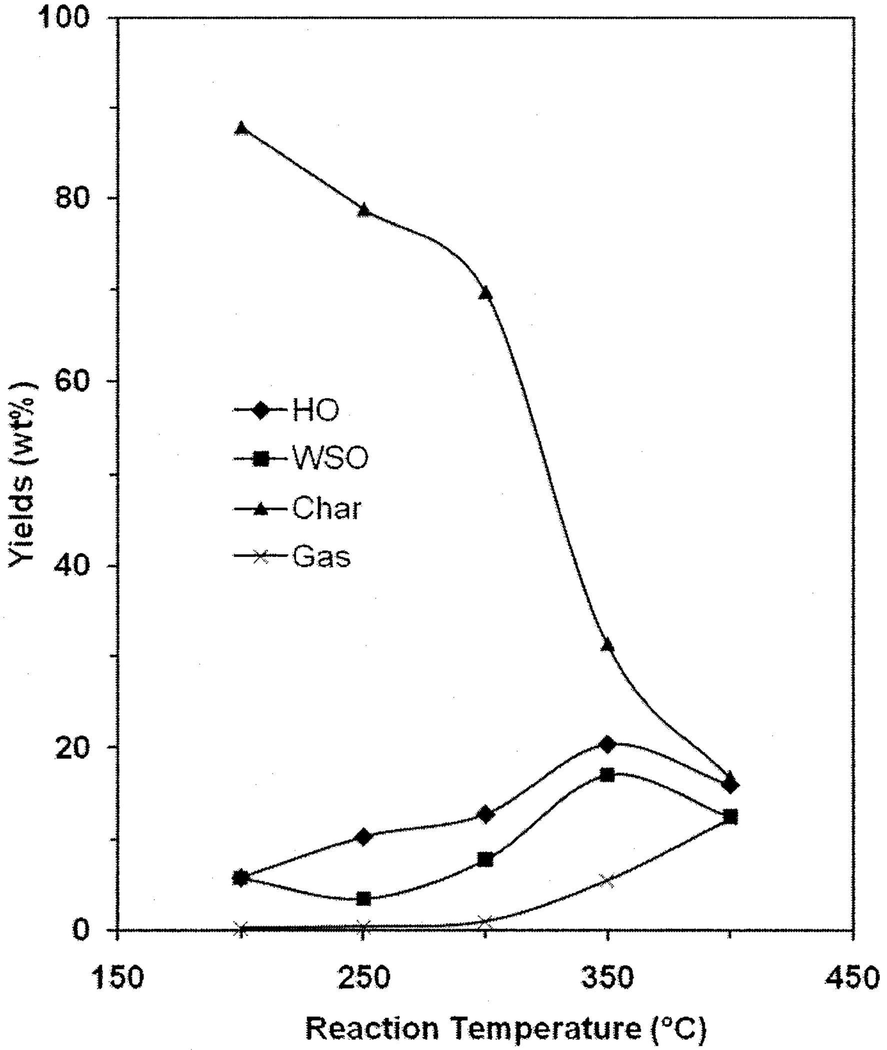


Figure 3-3. Yields of products as function of reaction temperature in hydro-liquefaction of birch powder in methanol without catalyst at various temperatures. Reaction conditions: Without catalyst; Reaction time of 30min; Solvent-to-Biomass ratio of 5; Initial H_2 pressure of 2 MPa.

3.3.3 Influence of reaction temperature

Effects of temperature on the liquefaction product yields can be shown from Figure 3-3, where the results were obtained from the experimental runs at various temperatures ranging from 200°C (sub-critical) to 400°C (supercritical), while under the same remaining conditions (2.0

MPa H_2, solvent-to-biomass ratio of 5:1, residence time of 30 min, and without catalyst). As clearly shown from the figure, the operation temperature significantly affected the biomass conversion process in hot-compressed methanol: The biomass conversion and the Gas yield increased continuously as the temperature increased from 200°C to 400°C, suggesting an enhanced decomposition of biomass and gas formation at a higher temperature. These effects were found to be more evident as temperature was above 300°C. The Gas yield climbed rapidly from 1 wt% at 300°C to 12 wt% at 400°C, accompanied by a drastic decrease in Char yield from 70 % at 300°C to as low as 16 wt% at 400°C. Over the tested temperature range (200-400°C), the yields of liquid products generally increased with increasing temperature, while the formation of HO and WSO attained a maximum yield of 20 wt% and 17 wt%, respectively, at about 350°C. As the operation temperature further increased to 400°C, the HO yield decreased to 16 wt%, and the WSO yield reduced to 13 wt%. It might be concluded that 350°C is the optimum operating temperature for hydro-liquefaction of birch powder in methanol. Similar experiment results were obtained by Minami et al.[13] in liquefaction of Japanese beech and Japanese cedar in supercritical methanol, and by Xu and Etcheverry[4] in liquefaction of a pine wood in ethanol. These previous studies have both demonstrated that 350°C appeared to be the optimal treatment temperature for liquefaction of woody biomass in supercritical alcohols. For the production of liquid oils from biomass by direct liquefaction using supercritical alcohols, a too high operation temperature is not preferred, not only because thermal cracking of alcohols may occur at 370°–380°C[17], but also because of the remarkably enhanced cracking/condensation/dehydration reactions of the oil intermediates and products at a high temperature. The greatly enhanced cracking/condensation/dehydration reactions of the oil intermediates/products in the process would result in a significantly higher gas yield as evidenced in Figure 3-3, formation of amorphous carbon as evidenced later by the XRD observation in Figure 3-8, and a greater formation of pyrolytic water. Unfortunately, the products of water and light ends (with low boiling points) were unrecoverable in this study due to the loss in the evaporation process for recovering the WSO and HO products, and thus the formation of pyrolytic water was unable to be quantified directly. Nevertheless, the total amount of pyrolytic water and light ends could be calculated indirectly from the mass balance in the operation. Based on the data given in Figure 3-3, the calculations showed the total amount of pyrolytic water and light ends was as high as 46 wt% at 400°C, compared with only 10 wt% at 300°C, suggesting greatly promoted dehydration and cracking reactions of the oil intermediates/products at a high temperature, as proposed above.

In addition to the liquid and total gas yields as discussed above in Figure 3-3, yields of various gas species during the liquefaction operations at different temperatures are given in Figure 3-4. Generally, the yields of all gas species increased with temperature due to the enhanced cracking and pyrolysis reactions. In the operations at a temperature lower than 300°C, the dominant species was CO_2 without significant formation of other species. The formation of CO_2 at low treatment temperatures is more likely a result of thermal cleavage of *carboxyl* group in the lignocellulosic structure by the following d*ecarboxylation* reactions:

$$\text{R-C(O)OH or} \quad \text{R-C(O)O-R'} \leftrightarrow \text{R-H} + CO_2 \text{ or R-R'} + CO_2 \qquad (1)$$

where, the R and R' stand for any possible functional groups derived from the lignocellulosic materials, such as alkyl, phenyl and hydroxyl groups. As temperature increased further to above 300°C, as shown in Figure 3-4, the dominant species became CO, followed by CO_2, CH_4 and (C_2+C_3) species. The reason that the formation of CO_2 was overtaken by CO at a higher reaction temperature is believed to be mainly related to the following carbon gasification reaction:

$$C+CO_2 \rightarrow 2CO \qquad \Delta H = 172 \text{ kJ/mol} \qquad (2)$$

The above reaction is endothermic, and hence it is thermodynamically favorable at a higher reaction temperature, leading to favorable conversion of CO_2 to CO. The methane and C_2+C_3 (ethylene, ethane and propane) began to form in the process at above 350°C, and the yield of methane increased dramatically from 0.07 mmol/g at 350°C to 0.43 mmol/g at 400°C, which is likely due to the the methanation reaction as follows:

$$3H_2+CO \rightarrow CH_4+ H_2O\ (g) \qquad \Delta H = -206 \text{ kJ/mol} \qquad (3)$$

H_2 might also form in the liquefaction process, but it was unable to quantify its yield because H_2 was used as the pressurizing gas and a reactant for the hydro-liquefaction process.

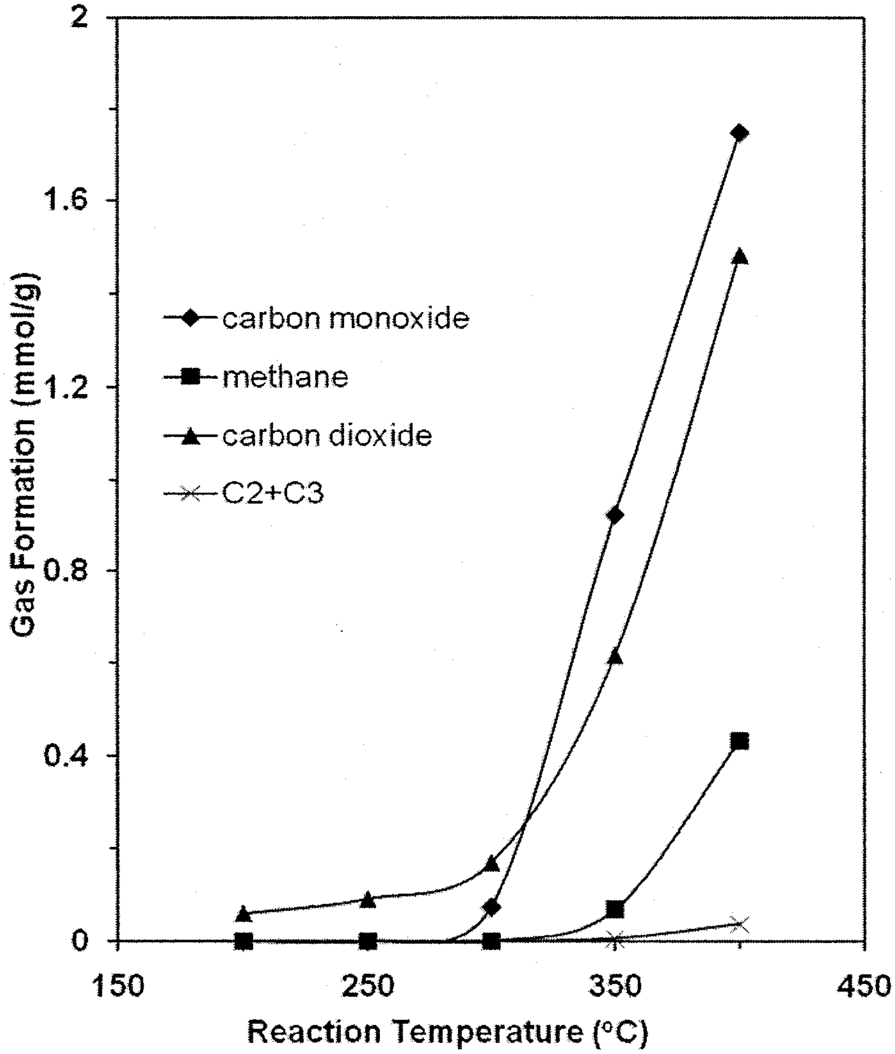


Figure 3-4. Yields of compositions of gases as function of reaction temperature in hydro-liquefaction of birch powder in methanol without catalyst at various temperatures. Reaction conditions: Without catalyst; Reaction time of 30min; Solvent-to-Biomass ratio of 5; Initial H_2 pressure of 2 MPa.

3.3.4 Influence of solvent-to-biomass ratio

Solvent-to-biomass ratio has been found as an important factor to influence biomass liquefaction in hot-compressed or supercritical water[27,28], where interestingly an decreased water-to-biomass ratio generally led to increased yields of heavy oil and char but a decreased yield of water soluble oil. For the operations with a smaller water-to-biomass ratio, a higher biomass concentration or a lower water concentration prevailed throughout the whole process, which might thus restrict the solvolysis/hydrolysis/hydration of the lignocellulosic solids, leading to a smaller yield of WSO and a higher yield of solid residue or Char. On the other hand, it is likely that a high biomass concentration or a low water concentration promoted the dehydration reactions of the WSO intermediates/products and the de-polymerization/cracking of the lignocellulosic solids leading to a greater yield of HO. For the biomass liquefaction operations in this study employing methanol and hydrogen, different from the previous work (using water and an inert atmosphere), it is thus necessary to examine the influence of solvent-to-biomass ratio. Effects of solvent-to-biomass ratio were investigated by conducting the liquefaction experiments for a reaction time of 30 min at 200°C and 300°C at various initial solvent-to-biomass ratios of 1, 2, 5 and 10. The results of product yields are illustrated in Figure 3-5. As clearly shown from the Figure, a higher WSO yield was observed at an increased solvent-to-biomass ratio, similar as that observed previously in the liquefaction of biomass with hot-compressed water[27,28]. In contrast, however, at both temperatures the solvent-to-biomass ratio did not show a significant influence on the liquefaction product yields except for the WSO yield, suggesting that in the present hydro-liquefaction process, solvent-to-biomass ratio was not a dominating factor affecting biomass conversion, compared to other factors such as hydrogen pressure, residence time and temperature as discussed earlier. The above result may be due to the unique solvolysis and transport properties of sub-/super-critical methanol, providing complete miscibility with the liquid/vapor products from the processes and a single-phase environment for reactions, thus minimizing the barrier of mass transfer that would otherwise be significant for a multiphase system[5].

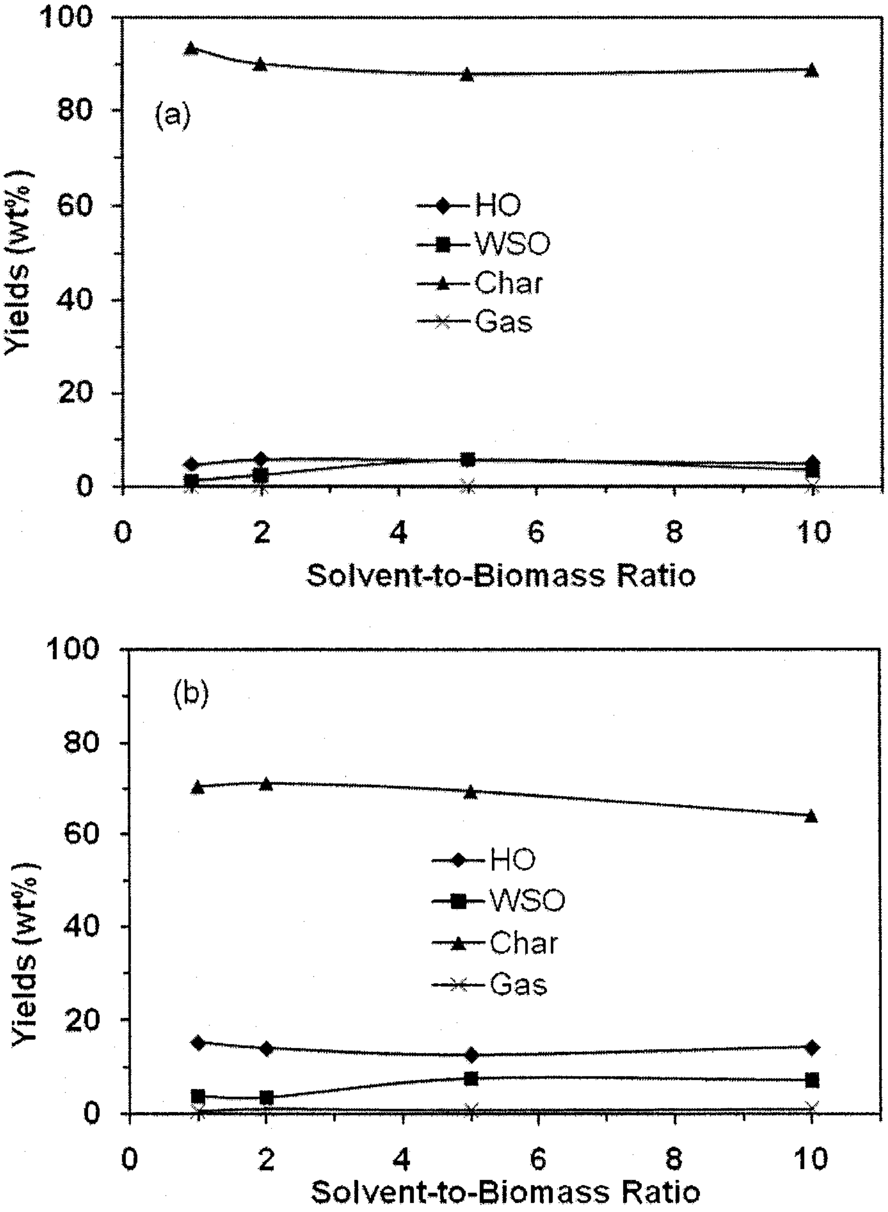


Figure 3-5. Yields of products as function of solvent-to-biomass ratio in hydro-liquefaction of birch powder in methanol at 200°C (a) and 300°C (b). Other reaction conditions: Without catalyst; Reaction time of 30min; Initial H_2 Pressure of 2 MPa.

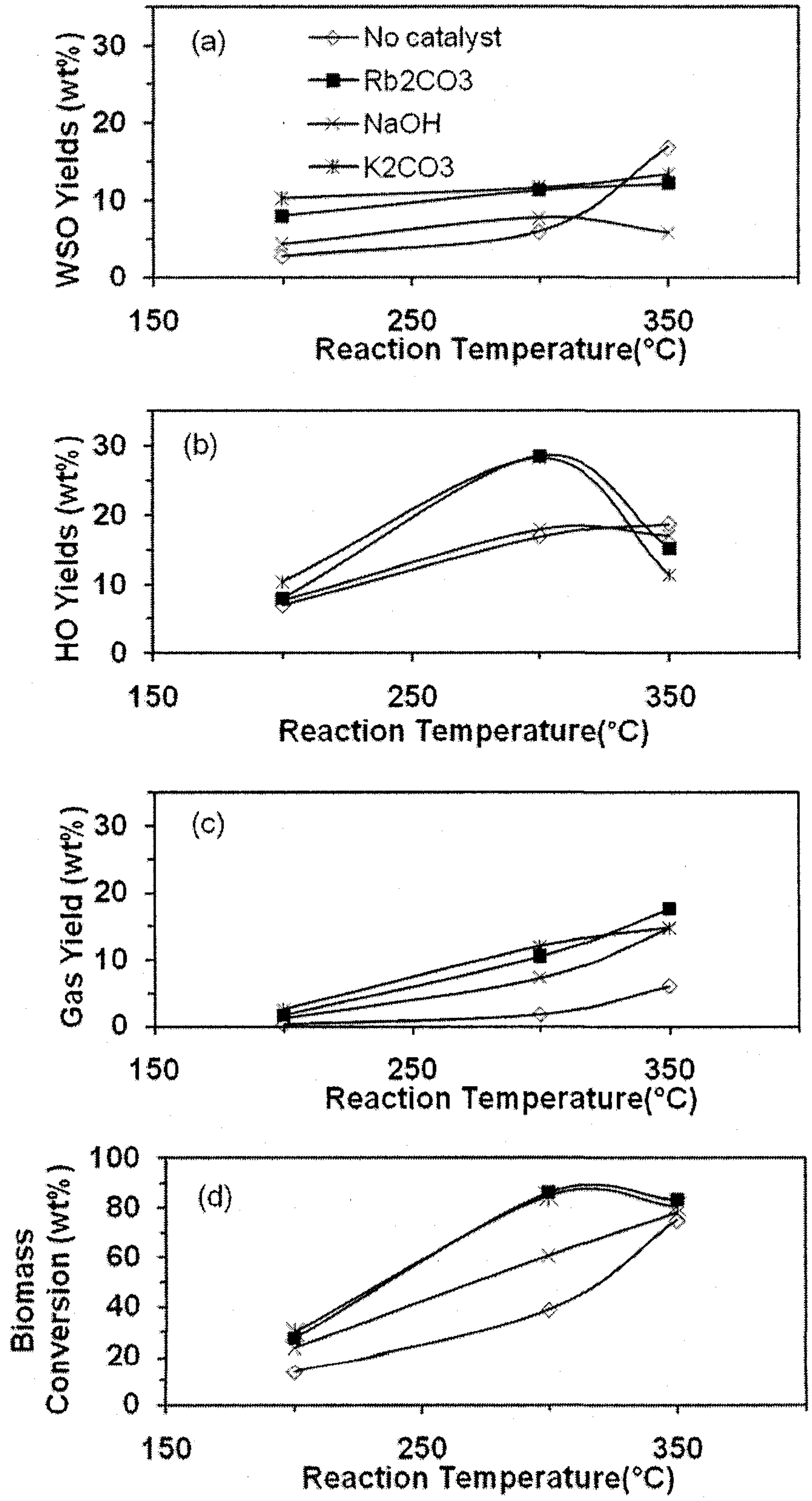


Figure 3-6. Effects of catalysts on yields of WSO (a), HO (b) and Gas(c) and biomass conversion (d) in hydro-liquefaction of birch powder in methanol (solvent-to-biomass ratio of 5) at various

temperatures for 60 min under H_2 of initial pressure of 2.0 MPa.

3.3.5 Effects of catalysts

Alkali metal compounds, e.g., Na_2CO_3, NaOH, K_2CO_3, KOH, RbOH and CsOH, etc., have been widely employed as catalysts in direct-liquefaction of agricultural/forest biomass to suppress the formation of char and to enhance the yield of liquid products[29-31]. A comparison of the yields of WSO and HO in hydro-liquefaction of birch powder in methanol for 60 min under H_2 of initial pressure of 2.0 MPa with and without catalyst (NaOH, K_2CO_3 and Rb_2CO_3) is given in Figures 3-6a and 3-6b. At a temperature between 200°C and 300°C, the yields of both oils were significantly improved by the use of all the catalysts. For all catalysts, their effects on HO formation were found to be more evident at a higher temperature, attaining a maximum at 300°C. As clearly shown in Figure 3-6, Rb_2CO_3 and K_2CO_3 were more effective than NaOH for enhancing the yields of either WSO or HO. At 300°C, the HO yield reached about 30 wt% with the presence of Rb_2CO_3 or K_2CO_3, almost double that of the operation without catalyst or with NaOH. However, as temperature increased to above 300°C the catalytic effects of all catalysts decreased significantly, and surprisingly the yields of both WSO and HO for the operations in the presence of all catalysts fell down to a level below that without catalyst. For instance, at 350°C, the HO yield decreased to 15 wt% and 11 wt% with the presence of Rb_2CO_3 and K_2CO_3, respectively, compared to 17 wt% without catalyst. Some reasons to account for these adverse effects of the catalysts on the yields of liquid products at 350°C shall be discussed. A comparison of the gas yield in the hydro-liquefaction operations with and without catalyst, as given in Figure 3-6c, describes the roles of the catalysts at a high temperature. Compared with the runs without catalyst, all runs with the presence the catalyst generated a much higher gas yield in particular when the temperature was higher than 300°C. At 350°C, the gas yield was increased remarkably from 6 wt% (without catalyst) to 15-18 wt% (with NaOH, K_2CO_3 or Rb_2CO_3). The formation of gas products in the operations with and without catalyst increased monotonically with increasing temperature, a trend that is different from those for WSO and HO products as shown in Figures 3-6a and 3-6b. Comparing Figures 3-6c with 3-6a and 3-6b for temperatures > 300°C, we may find that a remarkably increased gas formation due to the presence of the catalyst is accompanied by a drastic reduction in HO yield. This observation may suggest that the cracking reactions of HO products, thermodynamically favorable at a higher temperature, be catalyzed by the added catalysts, leading to a greatly reduced HO yield and a significantly enhanced gas formation, as evidenced by Figures 3-6b and 3-6c.

On the other hand, the effects of different catalysts on biomass conversion can be shown in Figure 3-6d, where a comparison of the biomass conversion in hydro-liquefaction of birch powder in methanol with and without catalysts is given. Compared with the operations without catalysts, the addition of all catalysts was effective for promoting biomass conversion at all temperatures in the range of 200-350°C, while the effects were found to be the most evident at 300°C and the effects remarkably dropped as the temperature increased to above 300°C, similar as those observed for HO yields in Figure 3-6b. At 300°C, the biomass conversion was increased remarkably from 39% (no catalyst) to 85% (with K_2CO_3 or Rb_2CO_3), while the use of the catalysts resulted in only a small increase in biomass conversion at 350°C. The declining activities for the catalysts on biomass conversion at a temperature higher than 300°C may be accounted for by the condensation/cracking reactions of WSO and HO products as discussed above. The catalyzed condensation and cracking reactions of the oil products at a high temperature > 300°C would lead to a remarked decrease in HO yield, a significantly enhanced gas formation and an increase in coke/carbon formation (which might thus result in a reduced value of biomass conversion), as evidenced by the Figures 3-6b through 3-6d. Another possible reason for the declining activities for the catalysts on biomass conversion at a temperature higher than 300°C might be related to the catalysts thermal degradation, which caused decomposition of the catalyst compounds (K_2CO_3 or Rb_2CO_3) or aggregation of the catalyst molecules (resulting in decreased surface areas of the catalysts). Theoretically, decomposition of K_2CO_3 or Rb_2CO_3 or aggregation of the catalyst molecules, if occurring during the treatment, would be able to verified by the XRD measurements of the resulted chars should different crystalline species (such as K_2O or Rb_2O) or increased crystalline sizes of K_2CO_3 or Rb_2CO_3 be observed. However, no crystalline species ascribed to the catalyst compounds were detected in our XRD measurement, as shown later in Figure 3-9, most likely because of the low loading amount (5 wt% of the biomass fed) for the catalyst compounds and possibly a high dispersion of the catalyst species on the resulted chars. From the above experiment results, it may be concluded that the optimal conditions for the production of bio-crude from woody biomass by hydro-liquefaction using supercritical methanol are: 300°C and with the presence of Rb_2CO_3 or K_2CO_3 as a catalyst.

3.3.6 Characterizations of the liquid/solid products

Carbon balance was calculated in this study in order to evaluate the material balance of the liquefaction operations. The carbon compositions of the liquefaction products (HO, WSO and Char) were analyzed with an elemental analyzer, and the carbon contents in the Gas products were obtained by GC-TCD. We defined the carbon recovery in a liquefaction product by the percentage of the moles of carbon in the product in relation to the moles of carbon in dried birch powder added to the reactor in the liquefaction operation. Some typical results of the carbon recovery in the products of HO, WSO, Char and Gas and the carbon balance calculated by summing the carbon recovery for all the products are presented in Table 3-2. As indicated in Table 3-2, the overall carbon molar conservation fell in a reasonable range of 80-92% in all operations, suggesting generally acceptable mass conservation and reliable experiment data. Compared with hydro-liquefaction operations with a catalyst, better carbon conservation was obtained for the operation without catalyst, when the carbon balance was as good as 92.3%. Relatively poor carbon balance was resulted from the liquefaction operation with Rb_2CO_3 or K_2CO_3. It is more likely due to the loss of some low boiling point light ends during the product separation process involving evaporation. As evidenced earlier in Figure 3-6, Rb_2CO_3 or K_2CO_3 was a very active catalyst to promote the formation of Gas and liquid products during liquefaction of the birch sample, when some low boiling point hydrocarbon compounds might form by decomposition of the lignocellulosic structures and by cracking of the liquid intermediates/products. This may be evidenced by a previous study by Karagoz et al.[30] on liquefaction of a woody biomass in hot-compressed water (280°C for 15 min), where liquid products were found to include $C_5 \sim C_6$ hydrocarbons of a boiling point ranging from 40°C~60°C.

Table 3-2. Carbon recovery in the products produced by hydro-liquefaction of birch powder at 300°C and 2.0 MPa H_2 for 60 min with and without catalyst

Liquefaction operation	Carbon recovery in products (%)				Carbon balance (%)
	HO	WSO	Char	Gas	
Without catalyst	24.60	6.50	59.83	1.22	92.15
Rb_2CO_3	42.61	12.83	16.21	7.64	79.29
K_2CO_3	43.31	17.55	14.94	8.55	84.35
NaOH	27.05	17.34	41.73	5.33	91.45

Properties of the heavy oil products are of a particular interest in this work. The elemental compositions (C, H and N) of some typical HO products are presented in Table 3-3, where the elemental compositions of the crude birch sample are 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 from the elemental analysis on a dry basis. Compared with the crude birch powder, all HO samples obtained from hydro-liquefaction of the birch powder have much higher contents of carbon and hydrogen, and lower concentrations of oxygen, leading to a significantly increased higher heating value (HHV). The HO products from the operations have a HHV of above 30 MJ/kg in relation to only 16 MJ/kg for the crude birch wood. Accordingly, with the maximum HO yield of about 30 wt% obtained from the treatment in the presence of 5 wt% Rb_2CO_3 or K_2CO_3 as shown in Figure 3-6, about 60% of the energy of the feedstock was recovered as the heavy oil (bio-crude) products. The result suggests that hydro-liquefaction in methanol with catalysts can be a promising technique (due to its relatively mild temperature conditions) for upgrading of woodwastes of a low-heating value to a liquid bio-crude with a significantly increased heating value. As also shown from the Table, all the bio-crude samples obtained with or without catalyst have very similar values of O/C (0.22 ~ 0.27) and H/C (1.2 ~ 1.3), both of which are much lower than those of the crude biomass feedstock (0.75 and 1.5, respectively), which may suggest high concentrations of phenolic or hydrocarbon compounds in the heavy oil products, as evidenced by the GC/MS results to be discussed below.

Table 3-3. Elemental compositions of the crude birch powder and the HO produced by hydro-liquefaction of the birch powder at 300°C and 2.0 MPa H_2 for 60 min with and without catalyst

Sample	Elemental compositions, wt% (d.b.)(1)				HHV (3) (MJ/kg)	O/C (-)	H/C (-)
	C	H	N	O (2)			
Crude birch powder	46.9	6.0	0.1	47.0	16.0	0.75	1.5
HO, no catalyst	68.5	6.7	0.1	24.7	28.3	0.27	1.2
HO, 5wt% NaOH	71.1	7.6	0.0	21.3	31.0	0.22	1.3
HO, 5wt% K_2CO_3	72.3	7.0	0.0	20.7	30.7	0.21	1.2
HO, 5wt% Rb_2CO_3	70.4	7.0	0.0	22.7	29.7	0.24	1.2

[1] On a dry basis;

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

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

Table 3-4. GC/MS analysis results for the heavy oils obtained in hydro-liquefaction of the birch powder in methanol under an initial H_2 pressure of 2.0 MPa at 300°C for 30 min (without catalyst) and 60 min (with catalysts)

RT (min)	Name	Area %			
		None	NaOH	K_2CO_3	Rb_2CO_3
4.882	2-Pentanone, 4-hydroxy-4-methyl-	1.7	5.39	5.76	1.91
11.113	1,2,3-Trimethoxybenzene		4.90	7.45	4.54
11.654	Phenol, 2,6-dimethoxy-	6.77	21.60	23.83	23.97
11.76	Phenol, 2-methoxy-4-propyl-			2.95	2.48
11.763	Phenol, 3,4-dimethoxy-		3.53		
12.092	Benzene, 1,2,3-trimethoxy-5-methyl-		1.14	2.15	1.44
12.582	Octanedioic acid, dimethyl ester		0.91	1.14	1.07
12.688	1,2,4-Trimethoxybenzene		7.41	4.32	4.54
12.778	Phenol, 2-methoxy-4-(1-propenyl)-	7.32			
12.87	Benzaldehyde, 3,4,5-trimethoxy-		2.76	3.75	
12.88	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-				2.4
13.444	5-tert-Butylpyrogallol	3.8	20.05	16.08	13.36
13.598	Nonanedioic acid, dimethyl ester	7	6.58	7.44	7.29
13.683	9H-Carbazol-3-amine, 9-ethyl-			1.26	0.99
13.956	3',5'-Dimethoxyacetophenone	3.03			
14.227	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	25.84			1.6
14.284	Benzene, 1,1'-propylidenebis-				7.96
14.282	2,4-Hexadienedioic acid, 3,4-diethyl-, dimethyl ester		12.84		
14.295	Benzene, 1-ethyl-3-(phenylmethyl)-			6.52	
14.548	1-Acetyl-4,6,8-trimethylazulene	1.55			
14.644	Isoelemicin		0.21		1.36
14.766	Benzene, 2-acetate-1,3-dimethoxy-5-(1-propenyl)	1.32			
15.01	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	4.65			
16.316	3,4,5-Trimethoxybenzyl methyl ether	4.30			
18.727	Hexadecanoic acid, methyl ester			3.36	3.97
18.788	9-Octadecenoic acid, 12-(acetyloxy)-, methyl ester	6.18			
23.622	9,12-Octadecadienoic acid, methyl ester			2.81	
23.634	10,13-Octadecadienoic acid, methyl ester				2.99
23.885	15-Octadecenoic acid, methyl ester	1.37			
24.496	Octadecanoic acid, methyl ester	7.9	3.26	4.47	5.62
25.846	Hexadecanoic acid, butyl ester	1.80			
26.639	Dodecanoic acid, 2-methyl-	1.60			
28.214	Eicosanoic acid, methyl ester	4.37	2.19	1.19	2.39
29.084	Octadecanoic acid, butyl ester	2.12			
29.64	Heneicosanoic acid, methyl ester	1.28			
30.807	Docosanoic acid, methyl ester	1.7	1.27	0.63	1.15
Total		**95.6**	**94.06**	**95.11**	**91.03**

The GC/MS analysis of heavy oil products obtained from the hydro-liquefaction of birch powder in supercritical methanol under initial pressure of H_2 of 2.0 MPa and 300°C for 30 min (without catalysts) and 60 min (with catalysts) were performed and presented in Table 3-4. The area % for each compound identified (defined by percentage of the compound's chromatographic area out of the total area) and the total area % for majority of the identified compounds are shown in the Table 3-4. It can be seen from Table 3-4 that the high proportions of phenol derivatives, followed by esters and benzene derivatives, such as 2,6-dimethoxy-phenol, 5-tert-butylpyrogallol, 4-hydroxy-4-methyl-2-pentanone, dimethyl ester nonanedioic acid, methyl ester octadecanoic acid and methyl ester eicosanoic acid were observed in all the HO samples tested, of which the concentrations of first two phenolic compounds were much higher in the samples obtained with catalysts than without catalyst. As shown in the Table, 2,6-dimethoxy-4-(2-propenyl)-phenol, 2-methoxy-4-(1-propenyl)-phenol and 12-(acetyloxy)-methyl ester 9-octadecenoic acid were the major compounds in heavy oils from the operation without catalyst, while most of these compounds were not detected by GC/MS in the HO products from the treatments with catalysts. As well known, the phenolic compounds were originated from the degradation of the lignin component in the lignocellulosic biomass feedstock[32]. Lignin is a natural polymer of three main lignin building blocks (structural monomers), i.e., p-hydroxy-phenyl-propanol, guaiacyl-propanol and syringyl-propanol, linked mainly by two types of linkages: condensed linkages (e.g., 5-5 and β-1 linkages) and ether linkages (e.g., β-O-4 and α-O-4), while the ether linkages are the dominant linkages between the three main lignin building blocks. A previous study by Minami et al.[12] using lignin model compounds indicated that the condensed linkages of lignin are more stable during treatment with supercritical methanol, than the β-ether and α-ether linkages, and degradation pathways of phenolic and non-phenolic β-*O*-4 lignin model compounds treated in supercritical methanol were shown as in Figure 3-7. Therefore, the phenol derivatives, esters and benzene derivatives as observed in the HO products are mainly resulted from decomposition/de-polymerization of lignin by cleavage of its ether linkages in supercritical methanol. Hardwood (such as birch used in the present study) lignin, which is known to have more ether linkages, is therefore more readily depolymerized and liquefied compared with softwood lignin[13].

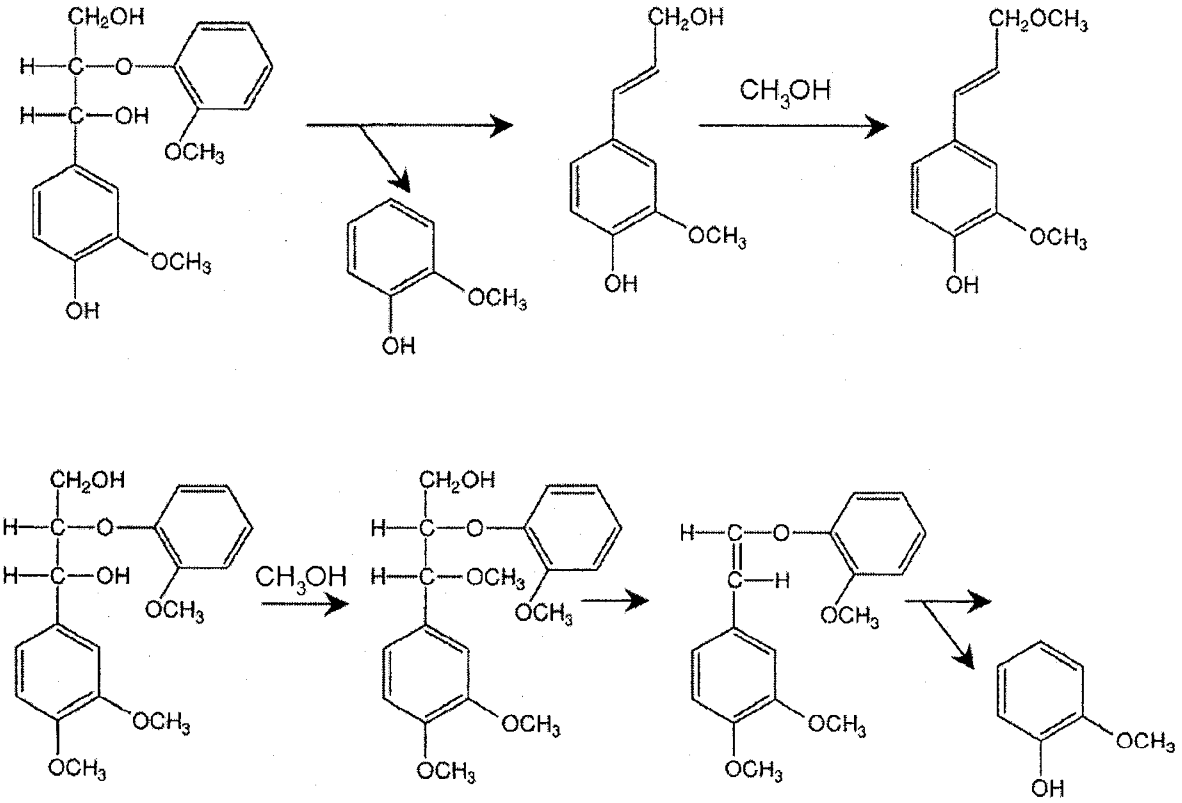


Figure 3-7. Degradation pathways of phenolic and nonphenolic β-*O*-4 lignin model compounds treated in supercritical methanol.[12]

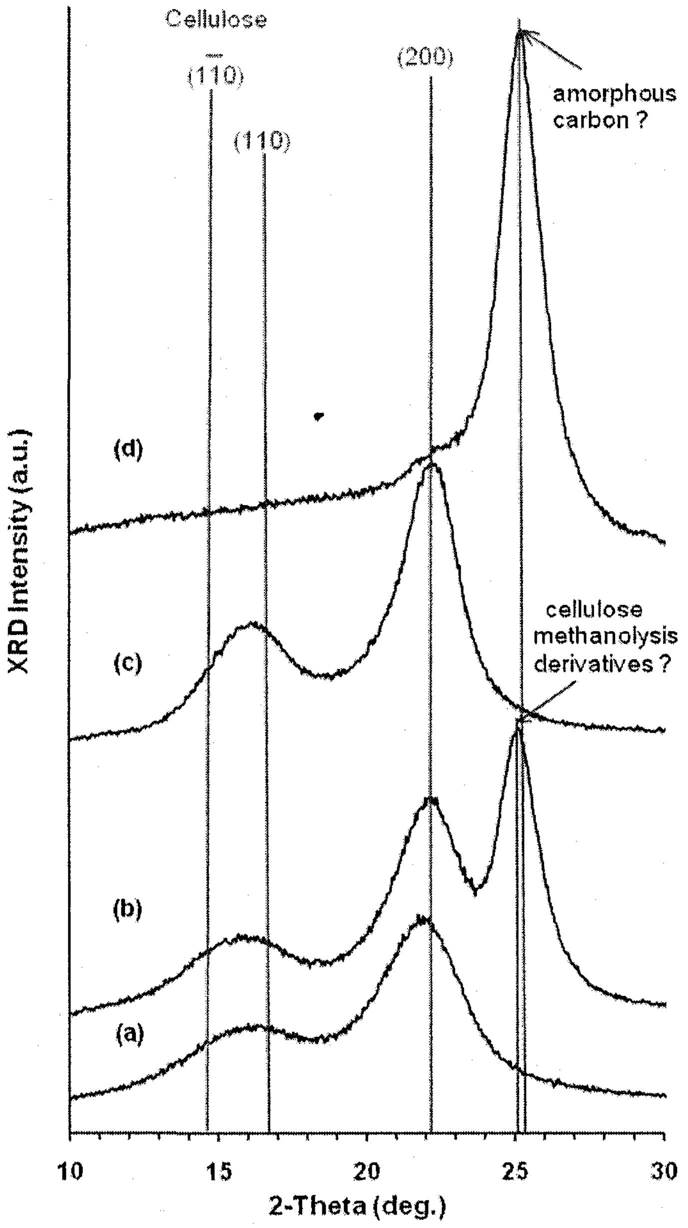


Figure 3-8 X-ray diffraction patterns of birch powder before and after liquefaction in methanol under H_2 of initial pressure of 2.0 MPa for 60 min at various temperatures without catalysts. (a) crude birch powder; (b)treatment at 200°C; (c) treatment at 300°C; (d) treatment at 400°C.

To examine the evolution of the crystalline forms in the wood samples and the dispersion states of the catalyst compounds, X-ray diffraction (XRD) measurements were carried out.

Figure 3-8 illustrates the XRD spectra of the birch wood sawdust before and after liquefaction in methanol under H_2 of initial pressure of 2.0 MPa at various temperatures ranging from 200°C to 400°C without catalysts. The X-ray diffraction pattern of the crude birch wood may be resolved into three peaks at 2θ of 14.6°, 16.5° and 22.4°, corresponds to the $(1\bar{1}0)$, (110) and (200) planes of cellulose-I[22, 33, 34]. After being treated at 200°C in methanol, the three peaks derived from cellulose I weakened, while a very strong XRD signal at $2\theta = 25.1°$ was detected, as shown in Figure 3-8. A similar XRD signal at $2\theta = 25.1°$ was reported in liquefaction of Jack pine wood in ethanol, which was attributed to the diffraction of cellulose acetates with a certain degree of substitution[4]. In the present situation, this strong XRD signal at $2\theta = 25.1°$ might be attributed to the diffraction of cellulose methanolysis derivatives formed by the interaction between cellulose and the methanol solvent. Ishikawa et al.[35] researched the chemical conversion of microcrystalline cellulose (avicel), cotton linter and dissolving softwood pulp in supercritical methanol and found that the main decomposition pathway of cellulose in supercritical methanol starts with methanolysis of cellulose producing methylated cellotriose and methylated cellobiose, which are further converted to methyl α- and β-D-glucosides. Methyl α- and β-D-glucosides are anomerized in supercritical methanol, however, these products may be decomposed further under prolonged treatment to other products such as 5-(Hydroxymethyl) furfural (5-HMF). As shown in the Figure 3-8, the peak of cellulose methanolysis derivatives disappears when the reaction temperature increased further to 300°C, which likely was resulted from further decomposition of cellulose methanolysis derivatives at this temperature. In the 300°C methanol-treated samples, the dominant X-ray diffraction peaks were observed at 14.6°, 16.0° and 22.4°, 2θ, typical of cellulose I. It should however be noted that the cellulose I detected at 300°C was more likely the cellulose I_β which has monoclinic two-train crystallite structure, a more disordered form of cellulose I than cellulose I_α that was observed in the crude wood without treatment[4]. As clearly shown in Figure 3-8, if further increasing the temperature to 400°C, there were strong X-ray diffraction lines at 2θ between 24 and 26° dominating the spectrum. These XRD signals might be attributed to the C(002) diffraction lines of amorphous carbon ($2\theta = 24.4$) and turbostratic carbon ($2\theta = 26.2$), suggesting formation of partially crystallized coke/carbon from the pyrolysis of lignocellulosic matrix or condensation of liquid intermediates/products at high temperatures. Similar observations of crystallization of carbon have been reported in some previous studies on hydrothermal treatment of biomass in near and supercritical water[31,36].

Figure 3-9 illustrates the XRD spectra of the birch wood sawdust after liquefaction in methanol under H_2 of initial pressure of 2.0 MPa at 300 °C with and without catalysts (NaOH, K_2CO3, Rb_2CO_3). First, no X-ray diffraction signals attributable to any a catalyst compound were detected in the chars from the treatment with the catalysts, which may suggest an excellent dispersion of the catalyst compound on the corresponding char. After treatment at 300°C in supercritical methanol, for all the operations with and without catalysts, the X-ray diffraction peaks were observed at $2\theta = 14.6°, 16.0°, 22.4°$, typical of cellulose I, while these peaks were relatively weaker in the chars from treatments with catalysts than those without catalyst. For the chars from the treatments with Rb_2CO_3 and NaOH, X-ray diffraction peaks of $2\theta = 25.1°$ that might be attributed to the diffraction of cellulose methanolysis derivatives were also observed, as observed in the char after treatment in methanol without catalyst at 200°C (Figure 3-8).

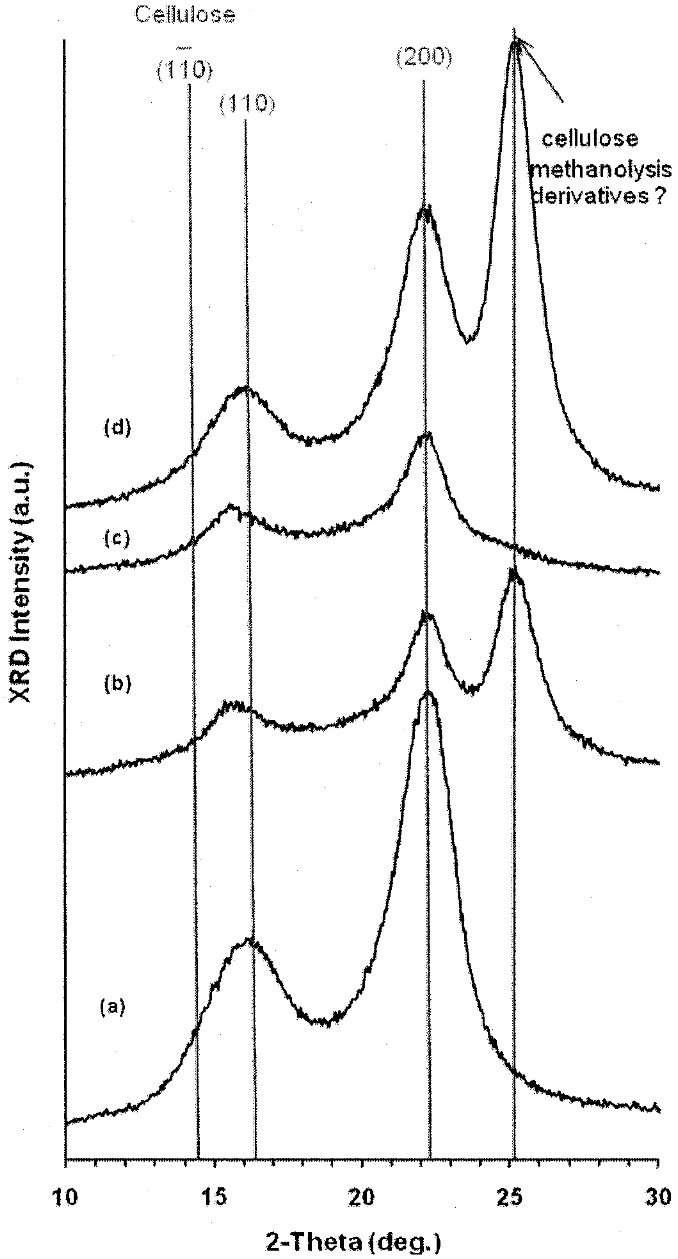


Figure 3-9 X-ray diffraction patterns of birch powder after liquefaction in methanol under H_2 of initial pressure of 2.0 MPa at 300°C for 60 min without and with catalysts: (a) without catalyst; (b) with Rb_2CO_3; (c) with K_2CO_3 ; (d) with NaOH.

3.4 Conclusions

In this study, high yields of heavy oil of a HHV > 30 MJ/kg were obtained by hydro-liquefaction of birch powder in sub-/super-critical methanol with and without catalyst at temperatures of 200°C-400°C in hydrogen of initial pressure of 2.0 MPa. The conclusions may be summarized as follows:

1) Longer residence time and lower initial H_2 pressure were found to be favorable conditions for the producing heavy oil products from biomass in sub-/super-critical methanol, while the optimal temperature for the heavy oil production appeared to be at around 350°C.
2) The addition of a basic catalyst of NaOH, K_2CO_3 or Rb_2CO_3 not only significantly enhanced biomass conversion or suppressed char formation, but greatly increased the yields of liquid and gas products, in particular when the operation temperature was lower than 300°C. Compared with NaOH, K_2CO_3 and Rb_2CO_3 showed higher catalytic activities. The yield of heavy oil attained about 30 wt% for the liquefaction operation in the presence of 5 wt% K_2CO_3 or Rb_2CO_3 at 300°C and 2 MPa of H_2 for 60 min.
3) Revealed by the GC-MS measurements, phenol derivatives, esters and benzene derivatives were the dominant compounds detected in the obtained heavy oil products, while their compositions could be altered by catalysts.
4) The HO products from the operations have a HHV of above 30 MJ/kg in relation to only 16 MJ/kg for the crude birch wood. Hydro-liquefaction in methanol can thus be a promising technique for upgrading of woodwastes of a low-heating value to bio-crude with a significantly increased heating value.

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CHAPTER 4

Hydrodeoxygenation of Bio-crude in Supercritical Hexane with Sulfided CoMo and CoMoP Catalysts Supported on MgO: A Model Compound Study Using Phenol*

Hydrodeoxygenation (HDO) of bio-crude was investigated using phenol as the model compound in supercritical hexane at temperatures of 300-450°C and initial pressure of hydrogen 5.0 MPa with MgO-supported sulfided CoMo with and without phosphorus as the catalyst promoter. The oily products after hydro-treatment were characterized by GC/MS and FTIR. Both MgO-supported catalysts proved to be effective for hydrodeoxygenation of phenol leading to significantly increased yields of reduced hydrocarbon products, such as benzene and cyclohexyl-aromatics, at temperatures higher than 350°C, while CoMoP/MgO showed superior activity in HDO of phenol. With the presence of CoMoP/MgO for 60 min and at 450°C, the treatment of phenol yielded a product containing approximately 65 wt% benzene and >10 wt% cyclohexyl-compounds. The fresh and spent catalysts were thoroughly characterized by ICP-AES, N_2 isothermal adsorption, XRD, XPS and TGA, and the roles of the phosphorus as the catalyst promoter and the effects of MgO as a basic support were also discussed.

Keywords: Bio-crude; Phenol; Hydrodeoxygenation; CoMo/MgO; CoMoP/MgO; Sulfided catalysts

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4.1 Introduction

Wood and wood residues can be good raw materials for the production of bio-fuels such as bio-oil or bio-crude, ethanol, syngas and Fischer-Trospch diesel, etc. Fast pyrolysis (high temperature process under inert atmosphere) and high-pressure direct liquefaction (mild temperature process with solvent under high pressure) are common thermo-chemical methods for conversion of woody biomass to liquid bio-fuels, i.e., bio-oils or bio-crudes. High-pressure direct liquefaction technology was found to be superior to the pyrolysis technology since it produces liquid oils with much higher caloric values (HHV = 30-35 MJ/kg) compared with only 20-25 MJ/kg for pyrolysis oils [1-3]. There are many successful researches reported on direct liquefaction of biomass in organic solvents such as anthracene oil [4,5] and alcohols [6,7] and hot compressed water [3,8,9]. A recent work by the authors [10] demonstrated that woody biomass (birch powder) was effectively liquefied into bio-crude in sub-/super-critical methanol without and with catalysts at temperatures of 200-400°C under H_2 of initial pressure of 2.0-10.0 MPa. The yield of heavy oil attained about 30 wt% for the liquefaction operation in the presence of 5 wt% Rb_2CO_3 at 573K and 2 MPa of H_2 for 60 min. The obtained heavy oil products consisted of a high concentration of phenol derivatives, esters and benzene derivatives, and they contained a heating value > 30 MJ/kg.

Bio-oils/bio-crudes comprise of a complex mixture of oxygen-containing compounds in the form of phenol derivatives, benzene derivatives, hydroxyketones, carboxylic acids and esters, and aliphatic and aromatic alcohols [3-10]. These compounds contribute to the oxygen content of the oil. In addition, water originating from both the moisture 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

[11,12]. 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 the process conditions, e.g. temperature, residence time, heating rate and different catalysts adopted [13,14]. The high oxygen content is a limitation for 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 (acidity) and immiscibility with hydrocarbon fuels [11,12,15]. Therefore, bio-crude must be upgraded by various means to reduce its oxygen content [14,16].

Technologies for upgrading of bio-oils for fuel applications includes physical and chemical/catalytic methods [17,18]. Techniques such as emulsification and solvent extraction are physical methods in which bio-fuels are mixed with diesel oil and solvents, respectively, to extract less oxygen-containing components from the original bio-oil [18]. Although physically mixing a bio-oil with diesel directly aided by addition some surfactant may be the simplest way to use bio-oil as a liquid transportation fuel, the accompanying corrosiveness to the engine and the subassemblies is inevitably serious.

Currently, two chemical methods have been proposed and tested for upgrading of pyrolysis oils and bio-crudes from direct liquefaction processes, analogy to upgrading of heavy oils in a petroleum refinery, i.e., catalytic cracking and catalytic hydro-treating. A catalytic cracking process, using cracking catalysts (zeolites, silica–alumina and molecular sieves), is performed at atmospheric pressure without the requirement of 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 literature [19–23]. The yield of hydrocarbons is however very low because of the high yields of char/coke and tar. Deposition of these undesired products on the catalyst would also cause serious problem of catalyst deactivation. As such, a periodical or continual regeneration of catalysts is necessary.

In contrast, the other chemical method, i.e., catalytic hydro-treating is operated under high pressure with hydrogen and/or in the presence of hydrogen donor solvents [24–26]. Over the past 20 years, significant efforts have been made in hydrodeoxygenation (HDO) of biomass-derived oils. Research efforts to study the catalytic chemistry and kinetics of hydrotreating various model compounds containing oxygen, such as phenolic compounds and aromatic ethers, have been recently reviewed by Furimsky [13] and Elliott [27]. Pacific Northwest National Laboratory (PNL/PNNL) employed a batch reactor to test hydro-treating of phenolic model compounds with various catalysts [28]. Some key results are summarized as follows. Commercial 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 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. concluded that NiMo with a phosphated alumina support was the most active for oxygen removal and hydrogen addition [29], but the authors pointed out that if hydrodeoxygenation is the main aim the CoMo catalyst shall be considered due to its much higher selectivity [29]. Addition a small amount of phosphorus in sulfided $NiMo/Al_2O_3$ catalyst has been shown to enhance both hydrodenitrogenation (HDN) and hydrodesulphurisation (HDS) activities, with less susceptibility to coke formation [30]. The addition of phosphorus to NiMo/Al_2O_3 led to the formation of acid centers with intermediate strength. Due to the addition of phosphorus to NiMo/Al_2O_3, new Lewis and Brönsted acid sites on the catalyst surface were evidenced by FTIR analysis [31]. Zhang et al. [32] hydrotreated a pyrolysis oil using sulfided CoMoP/γ-Al_2O_3, where the reaction was operated in an autoclave filled with tetralin (a common hydrogen donor solvent) under the optimum conditions of 360°C and 2 MPa of cold hydrogen pressure. The oxygen content was reduced from 41.8 wt% for the crude oil to 3 wt% for the upgraded product.

One of the key parameters determining the hydrodeoxygenation (HDO) activity of Mo, CoMo or NiMo catalysts is the type of support. The most common and conventional support is Al_2O_3, which has been widely used in hydro-treating catalysts on an industrial scale [33]. Extensive studies have been undertaken on CoMo and NiMo catalysts supported on alternative materials such as SiO_2, active carbon, TiO_2, ZrO_2, zeolites and various mixed oxides [34–38]. Centeno, et al. [39] 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 *para*-xylene medium. Initial studies showed that coke formation was an important cause for catalyst deactivation with the use of alumina support especially with compounds containing two oxygens such as guaiacols or catechols [39]. MgO as a basic support has attracted much less attention. Basic supports are however interesting for two main reasons as stated by Klicpera and Zdrazil [40]. First, the acid–base interaction between acidic MoO_3 and a basic support in the oxide precursors of the sulfided catalyst could promote dispersion of the Mo species in the catalyst. Second, the basic character of the support could inhibit coking which is rather intensive over the conventional Al_2O_3-supported catalysts. The most active Co(Ni)Mo/MgO catalysts were found to be 1.5–2.3 times more active than their Al_2O_3-supported counterparts for the hydrodesulfurization of thiophene [41].

Although a limited number of researches on sulfided MgO-supported catalysts have been reported in Journal literature [33, 42–50], catalytic application of the MgO supported catalysts to HDO of bio-crude or model is generally not available. In the present work, Hydro-treating of phenol as a model compound for bio-crude (bio-oil) was conducted by using sulfided MgO-supported catalysts in supercritical fluid of hexane at temperatures of 350-450°C under hydrogen atmosphere of an initial (cold) pressure of 5 MPa. Recently, supercritical hydrocarbon solvents such as decane, dodecane and hexadecane, paraffinic petroleum cuts, tetralin, decalin and toluene were used as effective hydro-treating reaction media for upgrading heavy oil or vacuum residua [51,52]. A supercritical fluid serves as not only a superb solvent to dissolve materials not normally soluble in either ambient liquid or vapor phase of the solvent, but an excellent reaction medium of complete miscibility with the gas and liquid/vapor products from the processes, providing a single-phase environment for reactions that would otherwise occur in a multiphase system under conventional conditions. An alkane (hexane, decane, dodecane, etc.) itself is not a hydrogen-donor, while at its supercritical state it has excellent solubility for hydrogen gas, and when combined with a suitable catalyst it could act as an effective hydrogen donor through a so-called "hydrogen shuttling" mechanism [51,52]. Hexane has a very low boiling point at 69°C and mild critical temperature and pressure of 235 °C and 3.1 MPa, which makes it a potential reaction medium for hydro-treating of bio-oils. A unique advantage of employing a low boiling-point hydrocarbon solvent as the reaction medium lies in the fact that it can be easily separated and recycled from the upgraded products by distillation.

4.2 Experimental

4.2.1 Materials and Catalyst Preparation/Characterizations

The phenol crystal sample and the n-hexane slovent used in this study were A.C.S. reagent-grade chemicals supplied from Sigma Aldrich and Canadawide Scientific, respectively. The chemicals were used as received.

As stated in the section of introduction, one of the objectives of the present work is to investigate on MgO–supported catalysts for hydrodeoxygenation of phenol in supercritical hexane. Nano-powder of MgO (with average particle size of 30 nm and a BET specific surface area of 60 m^2/g) was used as the catalyst support material. The supported metallic catalysts: 3%Co-13%Mo/MgO (CoMo/MgO in short) and 3%Co-13%Mo-2%P/ MgO (CoMoP/MgO in short) were synthesized by successive incipient wetness impregnation method with A.C.S. reagent-grade ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) and 86 wt% H_3PO_4 solution. The as-synthesized MgO-supported metallic catalysts were calcinated in air at 500°C for 5 hours, followed by sulfidation in a flow of 5% H_2S/H_2 at 400°C for 4h, and the resulted catalysts were crushed into fine particles of a particle size <300 μm.

Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was employed for measurement of the bulk compositions (molybdenum, cobalt and phosphorus contents) of the as synthesized sulfided catalysts. The analysis results are shown in Table 4-1. All the as-synthesized catalysts after sulfidation have a BET surface area of 40-51 m^2/g and a BJH desorption total pore volume of 0.12-0.16 cm^3/g, determined by N_2 isothermal (77K) adsorption (Micrometrics ASAP 2010 BET), as also given in Table 4-1. The as-synthesized catalysts after sulfidation were also characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (Philips PW 1050, 3710 Diffractometer). The fresh and spent catalysts were further characterized by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra X-ray photoelectron spectrometer, and by thermogravimetric analysis (TGA).

Table 4-1 Chemical compositions and textural properties of the fresh catalysts.

	Compositions[a] (wt%)				Surface area	Pore volume[b]
Sample	Mo	Co	P	MgO	(m^2/g)	(cm^3/g)
Co-Mo/MgO	8.3	2.1	0.0	84.9	45.5	0.15
Co-Mo-P/MgO	7.6	1.8	1.4	84.9	51.1	0.16

[a] Determined by ICP-AES;

[b] Single point adsorption total pore volume of pores less than 83 nm diameter.

4.2.2 Hydro-treatment Apparatus and Methods

All tests reported here were carried out in a high-pressure micro-reactor system whose details were given elsewhere [52]. 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, 1g of the phenol crystal was weighted into the reactor, followed by adding catalyst in an amount of 20 wt% (w/w) of the phenol crystal fed, and then 5g of the hexane solvent was added. The solvent/phenol crystal ratio was fixed at 5:1 (w/w). The air inside the reactor was displaced with ultra-pure hydrogen by repetitive operation of vacuuming and H_2-charging. Finally, the reactor was pressurized to 5.0 MPa of H_2. Supported on a mechanical shaker (set at 100 rpm), the reactor was then rapidly submerged in a fluidized sand bath pre-heated at the desired temperature for the reaction (300-450°C). After the predetermined reaction time, fixed at 60 min, has elapsed, the reactor was removed from the sand bath and quenched in a water bath to stop the reactions. Once the reactor was cooled to room temperature, the gas inside was collected in a gas bag (800 ml). The solid/liquid products were rinsed completely from the reactor with acetone into a beaker. The resulted mixture was filtered through a glass-fiber filter (Ahlstrom 111) to recover catalyst and acetone insolubles (coke or char). Then about 2.5g of anhydrous $MgSO_4$ was added to the filtrate to remove water produced during the reaction. The mixture was filtered again through a glass-fiber filter (Ahlstrom 111) to recover $MgSO_4.xH_2O$. The resulted filtrate was evaporated at 40°C under reduced pressure in a flask to completely remove the acetone solvent to obtain the upgraded oily products. Almost all the experimental runs were repeated 2-3 times, and the errors in the product yields between the runs under the same conditions were ensured within 5% of the yields. The yields of gaseous products and coke/char in all experimental runs are found to be very negligible, <1 wt%. As a result, the product yields are not reported in this work.

4.2.3 Analysis of the Hydro-treated Phenol Products

The compositions of gaseous products were determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. The liquid oily products from hydro-treatment of phenol were analyzed by a gas chromatograph equipped with a mass selective detector [Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC equipped with VF-5 ms column (5% phenyl 95% dimethylpolysiloxane, 30 m×0.25 mm×0.25 μm); temperature program: 40°C (hold 2 min) →190°C (12°C/min) → 290°C (8 °C/min, hold 20 min)]. Compounds in liquid products were identified by means of the NIST 98 MS library with the 2002 update. The liquid products were also analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to examine the change in functional groups, especially the oxygen containing groups like O–H group in phenol, during the treatment.

4.3 Results and Discussion

4.3.1 GC/MS analysis of the liquid products

Chemical compositions of the liquid products from hydro-treatment of phenol in supercritical hexane were analyzed by GC/MS. Fig. 4-1 illustrates the total ion chromatograms for the liquid products from the treatment under H_2 of initial pressure of 5.0 MPa for 60 min with CoMoP/MgO catalysts at various temperatures (between 300°C and 450°C). The chemical compounds identified by GC/MS spectra and the area % for each compound (defined by percentage of the compound's chromatographic area out of the total area) for the liquid products from the 60 min-treatment with CoMoP/MgO are summarized in Table 4-2. For comparison, the results for the liquid products obtained with CoMo/MgO at 350°C are also provided in Table 4-2. As clearly shown in the Fig. 4-1 and Table 4-2, the hydro-treatment of phenol in supercritical hexane with either CoMo/MgO or CoMoP/MgO catalyst could effectively convert phenol into some hydrodeoxygenation products including predominantly benzene, cyclohexyl-benzene and cyclohexyl-phenol. The 60 min-treatment of phenol with CoMo/MgO at 350°C resulted in a liquid product with 83.3% phenol, 3.2% cyclohexyl-benzene, 7.5% cyclohexyl-phenol, and a negligibly small amount of benzene (0.01%), as shown in Table 4-2. Compared with CoMo/MgO, the phosphorus-containing catalyst CoMoP/MgO was found to be much more active in HDO of phenol. The 60 min-treatment of phenol with CoMoP/MgO at 350°C produced a liquid product with significantly decreased phenol content (64.8%) and remarkably increased contents of the hydrodeoxygenation products of cyclohexyl-benzene (6.4%), cyclohexyl-phenol (13%) and benzene (13.2%). The enhanced HDO activity of CoMoP/MgO clearly owes to the presence of phosphorus additive in the catalyst. Phosphorus as a catalyst promoter for hydro-treating catalysts have been observed in other previous researches [31,32], where the roles of phosphorus were believed to be related with the formation of new Lewis and Brönsted acid sites on the Al_2O_3-supported catalyst surfaces. The roles of the phosphorus in the MgO-supported catalyst will be discussed in the following section (3.3).

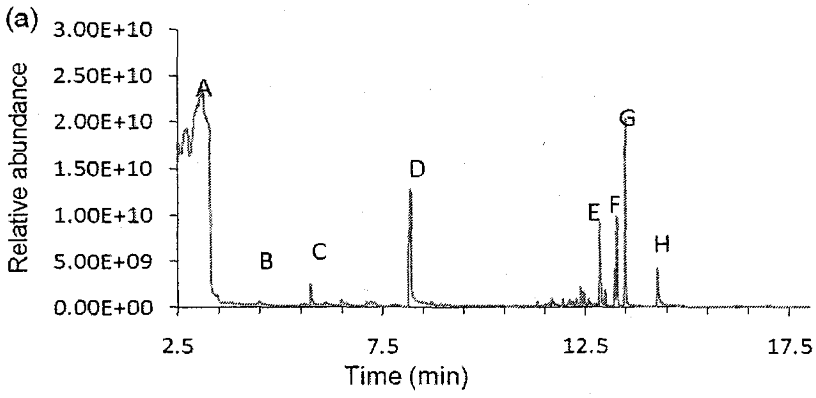
As clearly shown in Fig. 4-1 and Table 4-2, the concentration of phenol in the liquid products with the CoMoP/MgO catalyst decreased drastically with increasing the reaction temperature, from 98% at 300°C to 10.2% at 450°C, suggesting a deeper HDO of phenol at an elevated temperature. Benzene as the primary HDO product was only about 1% at 300°C, but it relative concentration increased to 13.23% at 350°C, 30% at 380°C and as high as 64% at 450°C. The concentrations of other main HDO products, i.e., cyclohexyl-benzene and cyclohexyl-phenol also increased as the hydro-treatment temperature increased from 300°C to 450°C, while they appeared to attain maximum at about 380°C. The concentrations of these phenol-derived bi-cyclic hydrocarbons decreased as the temperature increased further from 380°C to 450°C, accompanied by a sharp increase in benzene, suggesting hydro-cracking of these bi-cyclic hydrocarbons into benzene and saturated radicals. A previous study by Kallury et al. [53] obtained similar results by hydro-treating of phenol with MoO_3-NiO/Al_2O_3 catalyst at 450°C and 2.8 MPa hydrogen pressure for 45min, with formation of benzene (60%), cyclohexane (16%), and methylcyclopentane (7%) as the major products, followed by cyclohexylcyclohexane (2%), diphenyl (3%), and cyclohexylbenzene (2%). The authors also found that at lower temperatures (350 or 400°C) the conversion of phenol was not complete even after 2 h. The results from the present work as discussed above seem to be in a good agreement with the study by Kallury et al. [53] and another previous work by Cawley [54] where phenol was converted into cyclohexane and benzene at a yield of 37% and 25%, respectively, at 400°C, and 35% and 44%, respectively, at 450°C. The removal of a hydroxyl group from a phenol could be achieved by either direct elimination of the hydroxyl group by hydrogenolysis or by the thermal dehydration of a saturated or partly saturated cyclic alcohol formed by hydrogen addition to the aromatic ring. Although both reactions proceed in a competitive manner, the direct hydroxyl group elimination reaction is the preferred reaction pathway with $CoMo/Al_2O_3$ catalysts [55]. From the results of the present work, it may also be reasonable to assume that hydrogenolysis of phenol to benzene (direct elimination of the hydroxyl group) is the dominant reaction and it becomes much more favorable at a higher temperature. A mechanism proposed by Kallury et al.

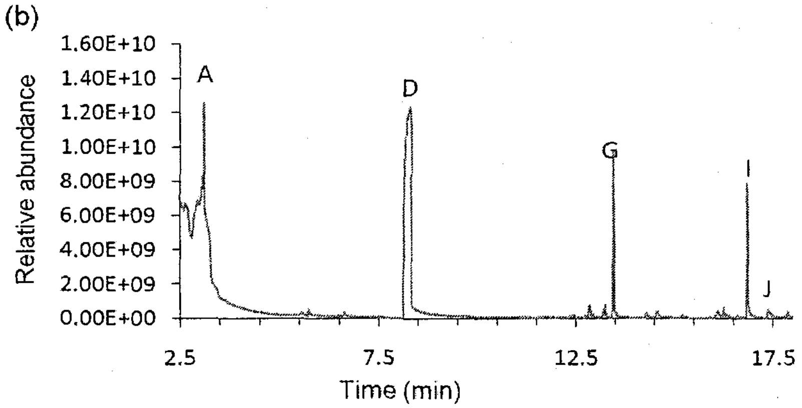
[53] may be adopted to explain these observations, as shown in Fig. 4-2. The pathway of phenol hydro-conversion involves hydrogenolysis of phenol to benzene and cyclohexanol as an intermediate/precursor to cyclohexane, methylcyclopentane, and the C_{12}-products.

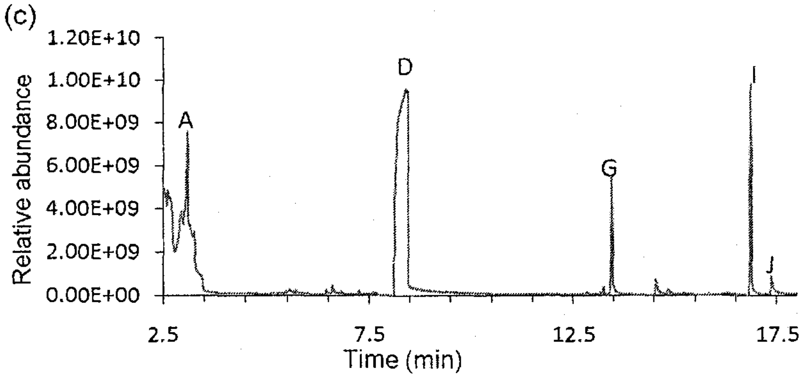
Table 4-2 GC/MS analysis results for liquid products obtained in hydro-treatment of phenol in supercritical hexane under an initial H_2 pressure of 5.0 MPa at different temperatures for 60 min.

Peak No.	RT (min)	Name	Area (%)			
			CoMo/MgO	CoMoP/MgO		
			350°C	350°C	380°C	450°C
A	3.061	Benzene	0.01	13.23	29.75	64.23
B	4.476	toluene				0.49
C	5.567	Cyclohexane, ethyl-				0.11
	6.094	Ethylbenzene				0.3
	6.453	Cyclohexanol	1.12			
	6.592	Cyclohexanone	0.75			
	7.112	Cyclohexane, (1-methylethyl)-				0.33
	7.197	Benzene, (1-methylethyl)-				0.34
	7.28	Cyclohexane, 2-propenyl-				0.35
D	8.593	Phenol	83.26	64.84	38.83	10.21
	8.707	Benzene, (1-methylpropyl)-				0.12
	11.302	Benzene, (1-ethylbutyl)-			0.03	0.17
	11.672	Benzene, (1-methylpentyl)-				0.32
E	11.945	Cyclohexane, (1-methylpropyl)-				0.34
	12.093	Benzene, cyclopentyl-			0.03	0.3
	12.274	Cyclohexane, hexyl-				0.29
	12.581	Benzene, hexyl-				0.31
	12.858	Cyclohexane, (cyclopentylmethyl)-				3.98
	13.202	Benzylcyclopentane			0.44	1.2
F	13.265	1,1'-Bicyclohexyl	0.09	0.14	0.55	2.91
G	13.476	Benzene, cyclohexyl-	3.21	6.36	10.04	7.57
H	14.269	Biphenyl			1.11	2.11
	14.56	Diphenyl ether	1.28	1.21	1.29	
	14.846	Benzene, (cyclohexyloxy)-	0.65	0.27	0.08	
I	16.873	Phenol, 2-cyclohexyl-	6.1	10.93	10.28	0.12
J	17.383	Phenol, 4-cyclohexyl-	1.49	2.04	2.16	

Total	97.96	99.02	94.59	96.1







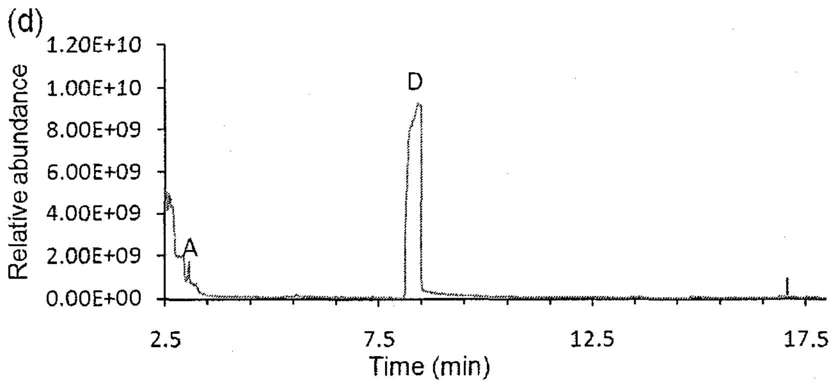


Fig.4-1. Total ion chromatograms of liquid products after hydro-treatment of phenol in supercritical hexane under H_2 of initial pressure of 5.0 MPa for 60 min with CoMoP/MgO catalysts at 450°C(a), 380°C (b), 350°C (c), and 300°C (d).

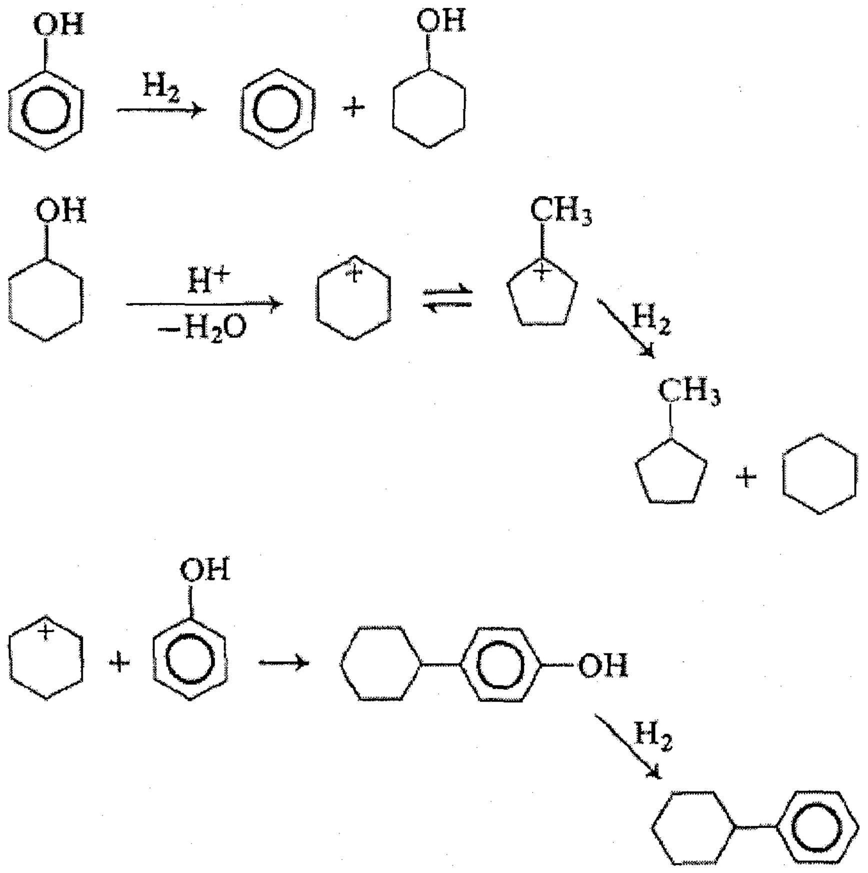


Fig.4-2. A possible phenol hydro-treating mechanism [53]

4.3.2 FTIR analysis of the liquid products

Fig.4-3 shows the FTIR spectra of the hydro-treated products from phenol at various reaction temperatures (300°C, 350°C and 380°C) with CoMoP/MgO catalyst. The stretching vibrations of hydroxyl (OH) group in the phenols and alcohols show characteristic adsorption in the region of 3700–3200 cm^{-1}, and the absorbance peaks between 1675 and 1500 cm^{-1} are due to stretching vibrations of C=C groups in aromatics. The absorptions between 1300 and 950 cm^{-1} may be attributed to the C–O stretching and O–H deformation vibrations existing in the primary, secondary and tertiary alcohols and phenols [56]. The absorbance peaks between 900 and 650 cm^{-1} are typical evidence for the presence of single, polycyclic and substituted aromatic groups. As shown from the FTIR spectra, the absorbance intensities at 3337 cm^{-1} ascribing to hydroxyl (OH) group in the phenols and between 1675 and 1500 cm^{-1} due to stretching vibrations of C=C groups in aromatics weakened with increasing temperature, suggesting hydrogenolysis of phenol and hydrogenation of aromatic HCs. As the strength of the absorption is proportional to the concentration, FTIR may be used for some quantitative analyses. The ratios of the strength of the absorbance peak of phenolic OH at 3337 cm^{-1} to that of the aromatic C=C groups at 1600 cm^{-1} were calculated to be 0.46 (300°C), 0.44 (350°C) and 0.38 (380°C), which may suggest a greater degree of HDO of phenol at a higher temperature.

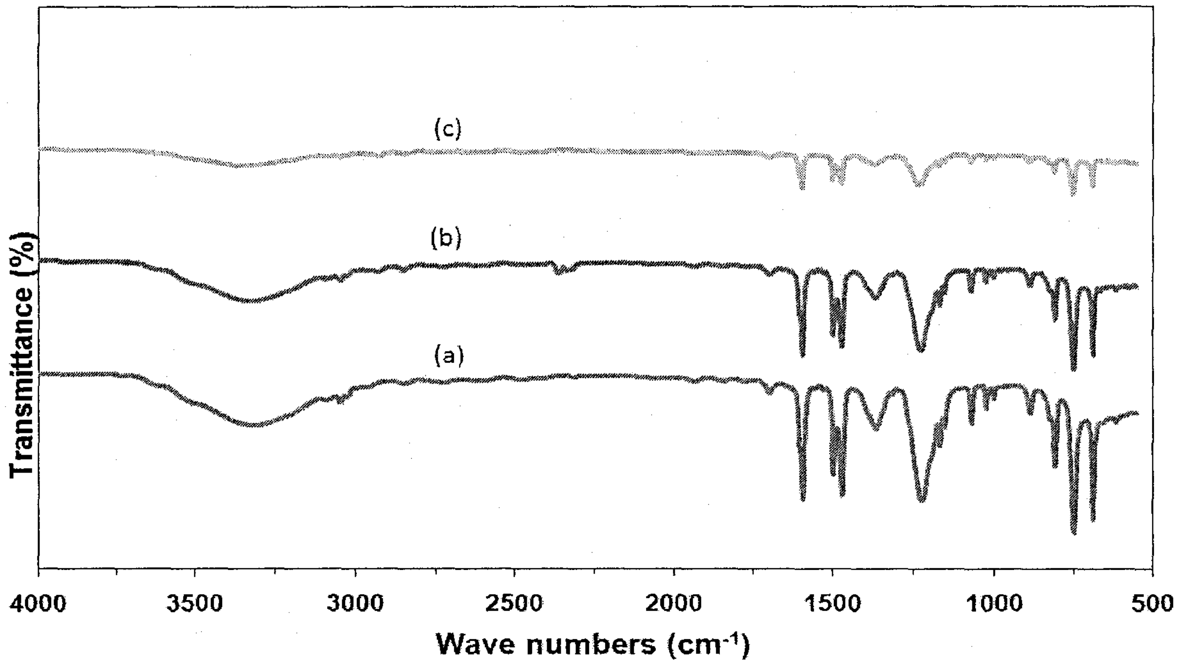


Fig.4-3. FTIR spectra of the hydro-treated phenol in supercritical hexane for 60 min with CoMoP/MgO catalyst at 300°C (a), 350°C (b) and 380°C (c).

4.3.3 Characterizations of Fresh and Spent Catalysts

The as-synthesized or fresh catalysts after sulfidation were characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (Philips PW 1050, 3710 Diffractometer), and the X-ray diffraction patterns of the fresh CoMoP/MgO and CoMo/MgO catalysts are illustrated in Fig. 4-4. As expected, diffraction lines of MgO as the catalyst support were the dominant signals detected in both samples. An interesting finding was that no XRD signals ascribable to Co-containing species and very weak signals of MoO_3 were found in both CoMoP/MgO and CoMo/MgO catalysts, suggesting very high dispersion of the metal species in these catalyst samples or the particles of the metal species are finer than 5 nm, below the XRD detection limited [57,58]. The high dispersion of the metal species in the MgO support might be accounted for by the basic property of the support which enhanced the interaction between the support and acidic metal species during the catalyst preparation, as demonstrated previously by many studies employing MgO as the support material in hydro-treating catalysts [33,59,60].

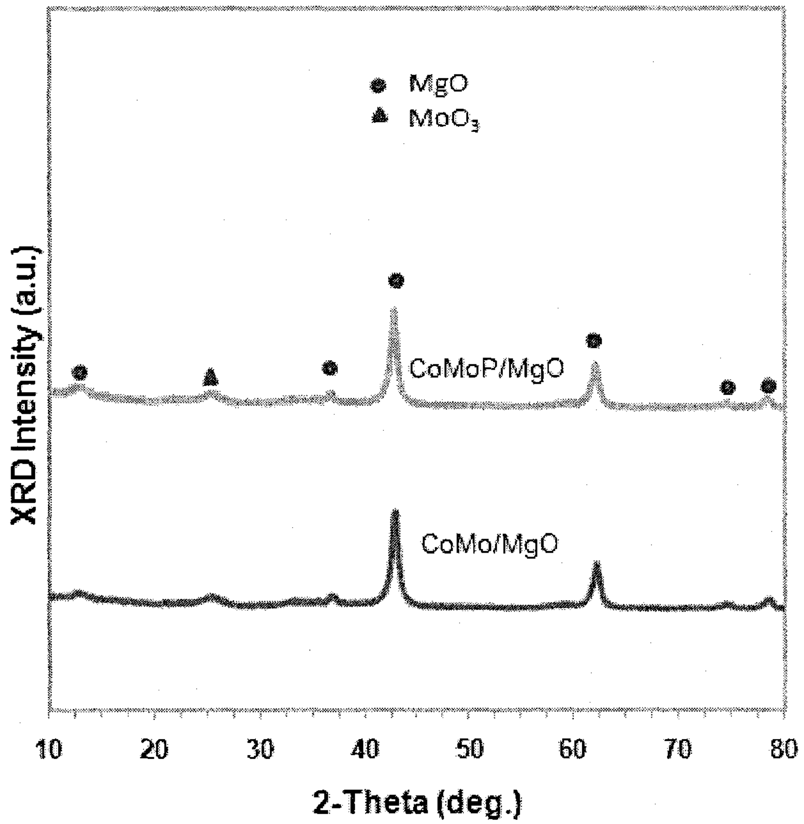


Fig.4-4. X-ray diffraction patterns for the as-synthesized catalysts of CoMo/MgO and CoMoP/MgO after sulfidation

Table 4-3 Surface compositions of the fresh and spent catalysts of CoMo/MgO and CoMoP/MgO determined by XPS analyses

	Atomic %						
Sample	Mo	Co	P	Mg	S	O	C
CoMo/MgO Fresh	2.2	0.5	0.0	15.6	2.9	47.2	31.60
CoMo/MgO spent[a]	1.7	1.0	0.0	21.7	3.0	48.9	23.70
CoMoP/MgO Fresh	2.4	0.8	0.7	18.4	3.2	52.6	21.90
CoMoP/MgO spent[a]	0.7	0.3	0.4	14.6	1.3	42.4	40.00

[a] Hydro-treatment conditions: 5.0 MPa H_2, 350°C and 60 min.

The samples of fresh and spent (after the hydro-treatment at 350°C for 60 min and 5 MPa H_2) CoMo/MgO and CoMoP/MgO were analyzed by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra X-ray photoelectron spectrometer. XPS survey spectra were obtained from an area of approximately 300 × 700 microns using a pass energy of 160 eV. Quantitative analysis of atomic ratios was accomplished by determining the elemental peak areas, following a Shirley background subtraction, and carried out using the sensitivity factors supplied with the instrument. Table 4-3 shows the surface composition (in atomic %) of the fresh and spent catalysts of CoMo/MgO and CoMoP/MgO determined by XPS. When comparing the two fresh catalysts, one might observe that the surface concentrations of all the elements (Mo, Co, Mg, S, O and C) are similarly. It shall be noted that the carbon detected in both fresh catalysts were resulted from the contamination of the samples. As expected, P was not detected on the surface of CoMo/MgO while it was observed at 0.7 atomic % in the CoMoP/MgO catalyst. Sulphur at 0.7 atomic % were observed in both samples. According to the S 2p spectra for both catalysts (fresh or spent), sulphur exists in the states of primarily S^{2-} (S 2p peak at around 160 ± 0.5 eV) resulted from the formation of MoS_2 during the sulfidation operation with H_2S [61,62]. Another S 2p peak observed at around 167 ± 0.5 eV in all samples may be ascribable to the sulfate species that could be formed by air oxidation of sample prior to or during the XPS measurements [61]. Compared with the fresh catalyst of CoMo/MgO, the atomic compositions of Mo in the spent catalyst reduced slightly from 2.2% to 1.7%, which might be due to the increases in the atomic contents of Co and Mg. The atomic composition of carbon in the spent catalyst of CoMo/MgO was found to be lower than that in the fresh one, suggesting good resistance to coke formation. For the phosphorus containing catalyst, CoMoP/MgO, compositions of all elements of Mo, Co, P, Mg, S and O in the spent catalyst reduced, which is likely due to the drastically increased carbon atomic % (from 22% in the fresh catalyst to 40% in the spent one). This may suggest coke deposition, resulted from the cracking/condensation reactions of phenol over the catalyst surface. Due to the influence from carbon contamination, the above discussion based on the surface carbon composition from the XPS analysis may not be necessarily true. As such, TGA measurement was employed for the spent catalysts to examine the extent of coke formation during the hydro-treatment of phenol with both catalysts, and the results will be discussed later in Fig.4-7.

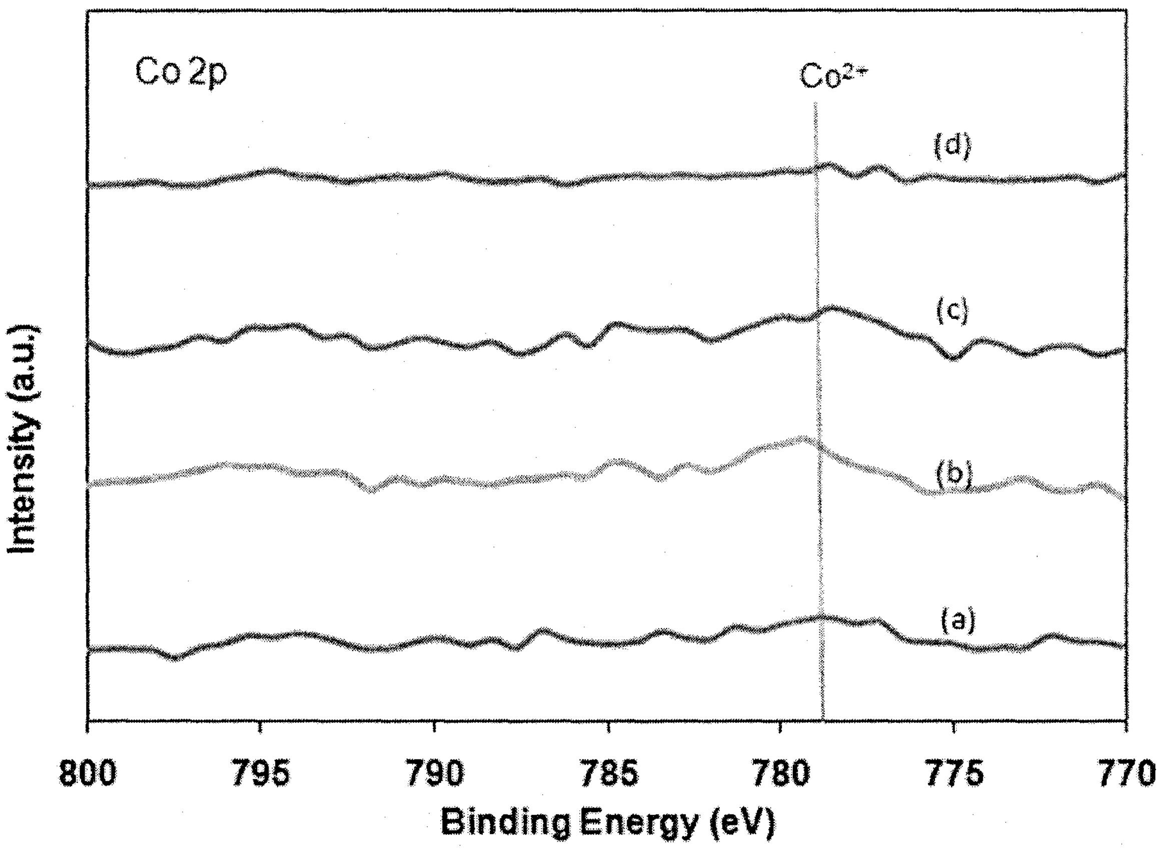


Fig.4-5. Co 2p XPS spectra for CoMo/MgO-fresh (a), CoMo/MgO-spent (b), CoMoP/MgO-fresh (c) and CoMoP/MgO-spent(d).

The XPS spectra of Co 2p for the fresh and spent catalysts of CoMo/MgO and CoMoP/MgO are shown in Fig.4-5. Very weak Co $2p_{3/2}$ peaks of binding energy at 778.6 eV were detected in all samples. Previous study by Alstrup et al. [63] showed that treatment of the $Co/SiO_2/Si(100)$ model catalyst in a mixture of H_2S and H_2 at room temperature or a higher temperature could completely convert cobalt in the sulfidic state, evidenced by the Co $2p_{3/2}$ binding energy of 778.2 to 778.6 eV. Even at room temperature, exposure of well dispersed cobalt oxide to H_2S would result in complete conversion of CoO to CoS [64]. In the present study, the calcinated CoMo/MgO and CoMoP/MgO catalysts were sulfided in a flow of $5\%H_2S/H_2$ at 400°C for 4 hours, which shall lead to complete conversion of Co to in CoS in both catalysts.

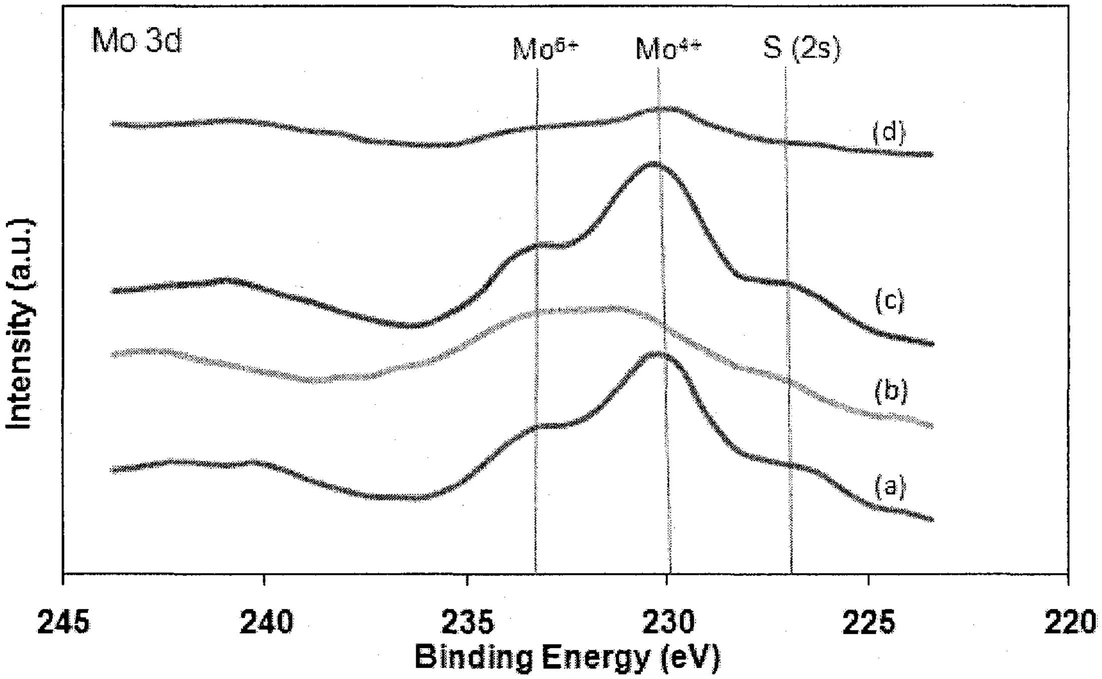


Fig.4-6. Mo 3d XPS spectra for CoMo/MgO-fresh (a), CoMo/MgO-spent (b), CoMoP/MgO-fresh (c) and CoMoP/MgO-spent(d).

Fig.4-6 illustrates the XPS spectra of Mo 3d for the fresh and spent catalysts of CoMo/MgO and CoMoP/MgO. The Mo 3d spectrum of the fresh CoMo/MgO and CoMoP/MgO consists of a doublet with binding energy between 228-234 eV, as shown in Fig.4-6. The shoulder peak at 232.6 ev is characteristic of Mo^{6+} in MoO_3 [65,66], and the main peak with binding energy of 229.0 eV may be ascribed to Mo^{4+} in MoS_2 [67–70]. The intensity of Mo^{4+} peak in the fresh CoMoP/MgO sample was found to be higher than that in the fresh CoMo/MgO catalyst. This may imply that the addition of phosphorus promoted the formation of MoS_2, the active sites of HDO reactions, which hence accounts for the much higher activity of CoMoP/MgO for HDO of phenol than that of CoMo/MgO, as discussed early in Table 4-2. The activity-promoting effects of phosphorus may be explained by the fact that (1) phosphorus could enhance the solubility of the molybdate by the formation of phosphomolybdate complexes, leading to a better dispersion of the Mo on the support, and (2) phosphorus would form compounds that are easily reducible and sulfidable [71,72].

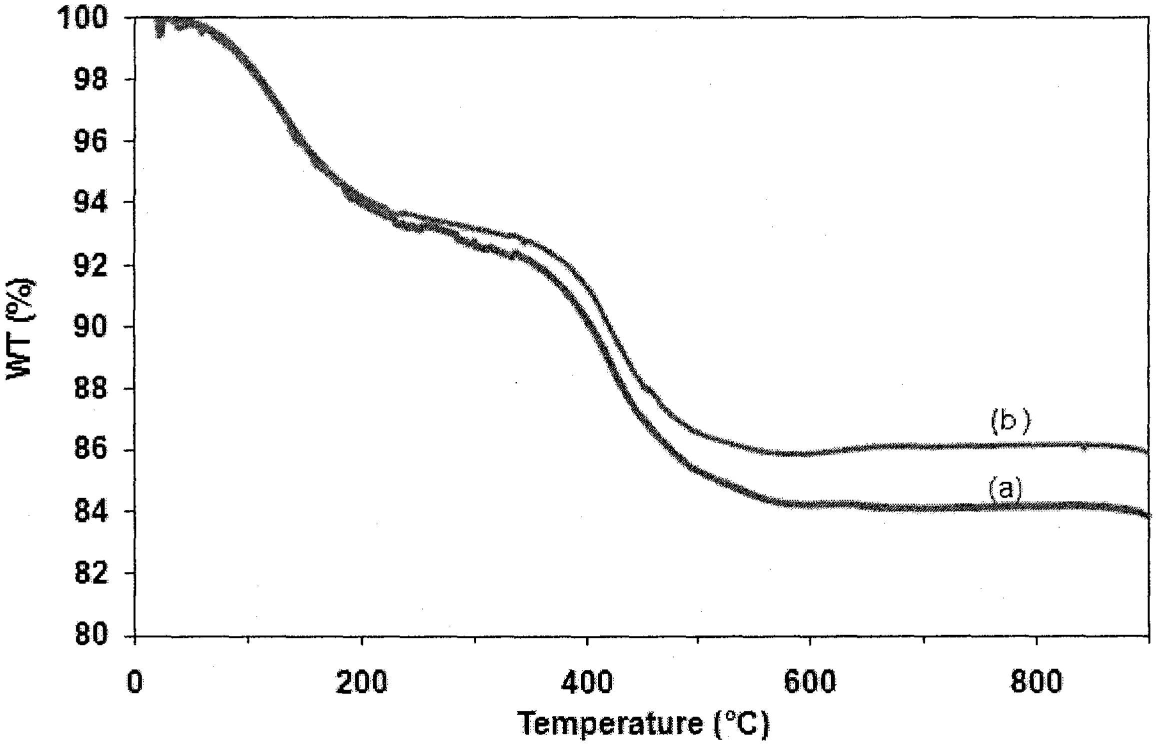


Fig.4-7. TGA profiles of the spent catalysts of CoMo/MgO (a) and CoMoP/MgO (b) after hydro-treatment of phenol in supercritical hexane under H_2 of initial pressure of 5.0 MPa for 60 min at 350°C.

In order to examine the extent of coke formation during the hydro-treatment of phenol with both catalysts, TGA measurement was employed for the spent catalysts. The TGA profiles of the spent catalysts of CoMo/MgO and CoMoP/MgO after hydro-treatment of phenol in supercritical hexane under H_2 of initial pressure of 5.0 MPa for 60 min at 350°C are illustrated Fig. 4-7. The TGA profiles were collected using the spent catalysts heated at 10 K/min from room temperature up to 900°C in 30 ml/min flow of air. The weight loss up to 200°C (of approximately 6 wt% for both catalysts) may be attributed to the removal of the water and lighter organics in the catalysts. The weight loss between 250 and 600°C may be attributed to the combustion of heavier residual coke and tar deposited on the catalysts. If evaluating the coke deposition by the weight loss between 250 and 600°C, the deposited amounts of coke in the spent catalysts of CoMo/MgO and CoMoP/MgO were 8 wt% and 10 wt%, respectively, as shown in Fig.4-7. This result may strongly suggest that the presence of a small amount of phosphorus in the CoMo/MgO catalyst could enhance the catalyst's resistance to coking which would hence promote its anti-deactivation ability. Our TGA results for both catalysts subject to hydro-treatment at a higher temperature also reveal less severe coke deposition. The superior resistance to coke deposition for the MgO-supported catalysts may be related with the basic character of the MgO support [41]: firstly, the oxide and sulfide Mo species are acidic and thus the basic support would keep them in a highly dispersed form as evidenced by the XRD measurement results (Fig. 4-4), and secondly, the basicity of MgO may promote formation of short edge-bonded MoS_2 slabs (each edge plane possesses Lewis acidity) and may thus increase the edge plane area suitable for the promotion by Co or Ni [33].

4.4 Conclusions

In this study, hydro-treating of phenol as a model compound for bio-crude were investigated in supercritical hexane at 300-450°C with novel MgO-supported sulfided CoMo and CoMoP catalysts.

The conclusions may be summarized as follows:

(1) Both MgO-supported catalysts proved to be effective for HDO of phenol in supercritical hexane at >350°C. The HDO activity of the catalyst was greatly promoted by addition of a small amount of phosphorus.

(2) The HDO of phenol may proceed with direct hydrogenolysis reaction and hydrogenation reaction involving cyclohexanol as an intermediate/precursor, resulting in conversion of phenol into benzene, cyclohexyl-aromatics and C_{12}-products. Hydrogenolysis of phenol to benzene (direct elimination of the hydroxyl group) is the dominant reaction and it becomes much more favorable at a higher temperature.

(3) The HDO activity of CoMoP/MgO increased drastically with increasing the reaction temperature. The hydro-treatment of phenol at 450°C with CoMoP/MgO catalyst led to a liquid product containing 10.2% phenol and 64% benzene.

(4) The superior resistance to coke deposition for the MgO-supported catalysts may be related with the basic character of the MgO support, and the presence of a small amount of phosphorus in the CoMo/MgO catalyst could further enhance the catalyst's resistance to coking.

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CHAPTER 5

Hydrodeoxygenation of Bio-crude in Supercritical Hexane with a Sulfided CoMoP Catalyst Supported on MgO*

Hydrodeoxygenation (HDO) of bio-crude derived from direct liquefaction of birch powder was investigated in supercritical hexane at temperatures of 300-380°C under hydrogen of a cold pressure of 2.0-10.0 MPa with MgO-supported sulfided CoMo with phosphorus as the catalyst promoter. The oil products were characterized by GC-MS, elemental analysis and FT-IR, and the fresh and spent catalysts by ICP-AES, N_2 isothermal adsorption, XRD, XPS and TGA. The hydro-treatment at temperatures higher than 350°C with the CoMoP/MgO catalyst proved to be effective for de-oxygenating the bio-crude sample, leading to significantly reduced contents of phenolic compounds and carboxylic acids/esters and greatly increased concentrations of oxygen-lean/free compounds such as ketones and hydrocarbons in the hydro-treated oil products. From the elemental analysis results, the upgraded oil products contained higher concentrations of carbon and hydrogen, and much lower concentrations of oxygen and nitrogen, resulting in an increased caloric values. For instance, the treatment at 350°C for 60 min under 5 MPa H_2 produced an upgraded oil with 0.2 wt% N, 16.1 wt% O and 34 MJ/kg HHV, compared with 0.6 wt% N, 26.2 wt% O and 27.1 MJ/kg HHV for the raw bio-crude.

Keywords: Bio-crude; Hydro-treatment, Hydrodeoxygenation; CoMoP/MgO catalyst; Sulfided catalysts

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* Manuscript (Yun Yang, Allan Gilbert and Chunbao (Charles) Xu) submitted to *AIChE Journal* for publication (under review).

5.1 Introduction

Pyrolysis and high-pressure direct liquefaction are two typical processes for production of bio-oil or bio-crude from biomass feedstocks. Fast pyrolysis (operating at a low/moderate pressure of 0.1-0.5 MPa and by heating the feedstock rapidly to a high temperature > 500°C in inert atmosphere) is so far the only industrially realized technology for production of bio-oils from biomass. However, pyrolysis oils consist of high oxygen contents (40-50 wt%) and hence lower caloric values and they are strongly acidic and corrosive. Superior to the pyrolysis technology, direct liquefaction technology with a suitable solvent (water or organics) and catalyst, which is normally operating at <400°C but high pressure of 5-20 MPa, has the potential for producing liquid oils (also called bio-crude) with higher caloric values and lower oxygen contents (<30 wt%). For use of bio-oils or bio-crude as a potential substitute for petroleum to produce liquid transport fuels, further treatment and upgrading of bio-crude is needed. Bio-crude upgrading can be realized by operations of catalytic cracking and hydro-treating, similar as those well-established in a petroleum refinery[1,2].

The oxygen content of bio-oils is a limitation for utilization as transport fuel since the high oxygen content causes high viscosity, poor thermal and chemical stability, corrosivity and immiscibility with hydrocarbon fuels[3-5]. Over the past 20 years, there have been significant efforts reported in hydrodeoxygenation (HDO) of biomass-derived oils. Research efforts in studying the catalytic chemistry and kinetics of hydro-treating bio-oils and various oxygen-containing model compounds (such as phenolic compounds and aromatic ethers) were recently reviewed by Furimsky[6] and Elliott[7]. Bio-oils are composed of a complex mixture of oxygen-containing compounds. These compounds contribute to oxygen content of the bio-oil in the form of phenolic compounds, hydroxyketones, aldehydes, carboxylic acids and esters, and aliphatic and aromatic alcohols. Previous researches developed a reactivity scale for different compounds in Bio-oil[8,9]. At low temperatures, reactive groups of olefins, aldehydes, and ketones are readily reduced by hydrogen, to stabilize the bio-oil. Alcohols can be reduced at 250-300°C by catalytic hydrogenation, but also by thermal dehydration to form olefins. At around 300°C, carboxylic and phenolic ethers can also be reduced. Reduction of phenols and di-phenyl ether needs a higher temperature of around 350°C, and reduction of dibenzofuran would take place at around 400°C.

Extensive studies have focused on using the conventional hyrdo-treating catalysts, i.e., sulfided CoMo and NiMo catalysts to upgrade bio-oil. Elliott et al.[10,11] examined the hydrocatalytic reactions of bio-oils from high pressure liquefaction in a continuously fed fixed bed reactor. Preliminary results showed that the sulfided form of the CoMo catalyst was much more active than the oxide form. The NiMo catalyst exhibited a similar activity as the CoMo catalyst, but it produced a much higher gas yield. A high oxygen removal efficiency, > 95%, was obtained in treating a bio-oil (containing about 15 wt.% O) produced from direct liquefaction of wood over a sulfided $CoMo/Al_2O_3$ catalyst at 300°C [12]. Using the same bio-oil, Gevert et al.[13] studied the effect of pore diameter of a sulfided $CoMo/Al_2O_3$ catalyst on the overall HDO. The best performance was achieved at 350°C for the catalyst with narrow pores. Churin et al.[14,15] reported upgrading experiments for pyrolysis oil from olive oil, where the authors found out that only sulfided NiMo or CoMo supported on alumina or silica-alumina supports would work for the HDO reactions. They claimed that the supported noble metal catalysts could be readily deactivated by the chemical and physicochemical processes such as poisoning, sintering, and fouling. The use of hydrogen donor solvent (such as tetrahydronaphthalene or tetralin) could result in a marked improvement of the quality of the products, and the catalysts are less deactivated by coke deposition. Piskorz et al.[17] reported hydrotreating pyrolytic lignin containing

18.0% moisture, extracted from fast-pyrolysis oil from softwood, with an unspecified Katalco sulfided CoMo pellet as the catalyst. The resulted light organic products had an H/C ratio of 1.50 and a very low oxygen content of 0.46 wt%. Zhang et al.[18] hydrotreated water-free fast pyrolysis oil using sulphided CoMoP/γ-Al_2O_3 in an autoclave filled with tetralin under the optimum conditions of 360°C and 2 MPa of cold hydrogen pressure. The oxygen content was reduced from 41.8% of the raw oil to 3% of the upgraded light fraction.

Although sulfided CoMo and NiMo catalysts are the most commonly used hydrotreating catalysts, other types of catalysts, such as solid acids and solid bases, and different metals or metals supported on non-acidic materials (such as carbon or MgO, etc.), have also been tested for HDO of bio-oil. Zhang et al.[19] investigated upgrading of fast pyrolysis oil with catalysts of a solid acid ($40SiO_2/TiO_2$-SO_4^{2-}) and a solid base ($30K_2CO_3/Al_2O_3$-NaOH) at 50°C for 5 h, where dynamic viscosities of bio-oil were found to be lowered markedly, the density of the oil was reduced from 1.24 to 0.96 kg/m^3, and the gross calorific value increased from 16 MJ/kg to 24 MJ/kg. Their results of GC/MS analysis showed that both solid acid and solid base catalysts could enhance the HDO reactions of the esters in the bio-oil. Elliott et al.[20] performed HDO tests on a softwood-derived bio-oil and a bagasse-derived bio-oil over a carbon-supported ruthenium catalyst. The softwood-derived oil appeared to be more readily hydrogenated than the bagasse-derived bio-oil. As reported by Gagnon and Kaliaguine[21], however, severe polymerization occurred during pre-treatment of vacuum pyrolysis oil over Ru/Al_2O_3 catalyst at 80°C and 4.2 MPa of H_2, leading to an increase in the molecular weights of the products. Polymerization was more evident during the subsequent hydro-treating process in the presence of a $NiWO/Al_2O_3$ catalyst at 325°C and about 18 MPa of H_2, although significant removal of oxygen was achieved. Soltes and co-workers[22,23] upgraded pyrolytic oil in batch and continuous-flow reactors, where

20 catalyst formulations were tested. On the basis of the testing results in a batch reactor at 400°C for 1 h, the alumina-supported Pd was shown be the most useful with respect to the highest liquid yield, while the alumina-supported other noble metals such as Pt, Re, Ru and Rh, although being useful, produced a much higher gas yield. Sulfided CoMo, NiMo, and NiW catalysts were however found to be less active than the noble metal catalysts, and the Pt catalyst was found to be the most active catalyst for oxygen removal. Utilisation of these noble metal catalysts rather than CoMo and NiMo in bio-oil upgrading is, however, much expensive.

The extensive application of sulfided CoMo and NiMo catalysts in petroleum refineries and their relatively lower costs still make them the most favourable catalysts for bio-oil upgrading. CoMo catalysts supported on non-acidic materials such as activated carbon have been tested for HDO by Ferrari et al.[24,25], and the carbon-supported catalysts showed better selectivities and less deactivation of the catalysts than the conventional Al_2O_3-supported catalysts. In addition to the carbon support, basic supports such as MgO have attracted much interest recently for HDO. Basic supports are interesting mainly for two reasons as stated by Klicpera and Zdrazil[26]. First, the acid–base interaction between acidic MoO_3 and a basic support in the oxide precursors of the sulfided catalyst could promote dispersion of the Mo species in the catalyst. Second, the basic character of the support could inhibit coking which is rather intensive over the conventional Al_2O_3-supported catalysts. Although quite a few researches on applications of MgO-supported catalysts have been reported in literature[26-30], catalytic application of MgO supported catalysts to HDO of bio-oil is not available. In accordance to our previous research in hydro-treating phenol as a model compound for bio-oils in supercritical hexane with MgO-supported sulfided CoMo and CoMoP Catalysts, it was demonstrated that CoMoP/MgO could be a very active catalyst for HDO. Phosphorus as a catalyst promoter for hydro-treating catalysts have been observed in other previous researches[18,27], where the roles of phosphorus were believed to be related with the formation of new Lewis and Brönsted acid sites on the Al_2O_3-supported catalyst surfaces.

In the present work, hydro-treating of bio-crude from direct liquefaction of birch wood was conducted using MgO-supported sulfided CoMoP Catalyst in supercritical fluid of hexane at a temperature between 300 and 380°C under hydrogen of a cold pressure varying from 2.0 to 10.0 MPa. The originality of the present work is the use of supercritical hexane as the hydro-treatment medium and magnesium oxide as support for the active catalytic phase (sulfided Co and Mo metals) modified by addition of phosphorus in the catalyst composition.

5.2 Experimental

5.2.1 Catalyst preparation/characterizations

Nano-powder of MgO (with average particle size of 30 nm and a BET specific surface area of 60 m^2/g) was used as the catalyst support material. The supported metallic catalyst: 3%Co-13%Mo-2%P/MgO (CoMoP/MgO in short) was synthesized by successive incipient wetness impregnation method with A.C.S. reagent-grade ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$) and 86 wt% H_3PO_4 solution. The as-synthesized MgO-supported metallic catalysts were calcinated in air at 500°C for 5 hours, followed by sulfidation in a flow of 5% H_2S/H_2 at 400°C for 4h, and the resulted catalysts were crushed into fine particles of a particle size <300 μm. The as-synthesized catalyst CoMoP/MgO after sulfidation was characterized by powder X-ray diffraction (XRD) using Cu Kα radiation (Philips PW 1050, 3710 Diffractometer), and the diffraction pattern is illustrated in Fig.5-1. As expected, diffraction lines of MgO as the catalyst support were the dominant signals. An interesting finding was that no XRD signals ascribable to Co-containing species and very weak signals of MoO_3 were detected in the sulfided CoMoP/MgO catalyst, suggesting very high dispersion of the metal species in the catalyst sample or the particles of the metal species are finer than 5 nm, below the XRD detection limit[31,32]. The high dispersion of the metal species in the MgO support might be accounted for by the basic property of the support which enhanced the interaction between the support and acidic metal species during the catalyst preparation, as demonstrated previously by many studies employing MgO as the support material in hydro-treating catalysts[30,33,34].

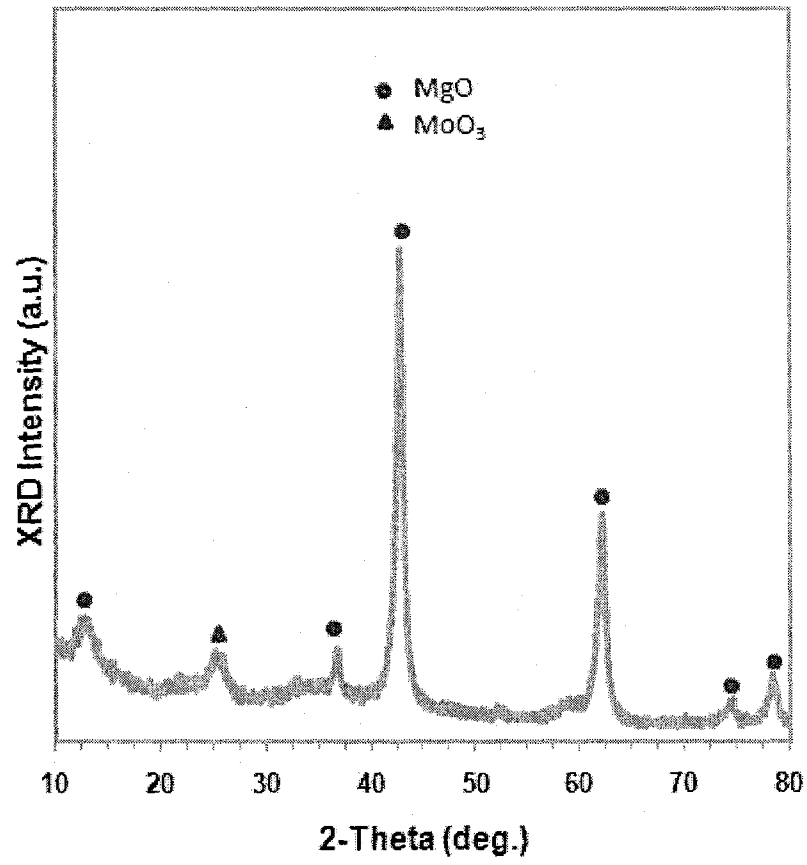

Fig.5-1. X-ray diffraction patterns for the as-synthesized catalysts of CoMoP/MgO after sulfidation.

Table 5-1

Chemical compositions and textural properties of the fresh catalyst.

Sample	Compositions[a] (wt%) Mo	Co	P	MgO	Surface area (m^2/g)	Pore volume[b] (cm^3/g)
Co-Mo-P/MgO	7.6	1.8	1.4	84.9	51.1	0.16

[a] Determined by ICP-AES;

[b] Single point adsorption total pore volume of pores less than 83 nm in diameter.

The inductively coupled plasma-atomic emission spectroscopy (ICP-AES) was employed for measurement of the bulk compositions (molybdenum, cobalt and phosphorus contents) of the as-synthesized sulfided CoMoP/MgO catalyst. The analysis results are shown in Table 5-1. The bulk compositions of the sulfided catalyst determined by the ICP-AES measurement are: 1.8 wt% Co, 7.6 wt% Mo and 1.4 wt% P. The as-synthesized catalyst has a BET surface area of 51 m^2/g and a BJH desorption total pore volume of 0.16 cm^3/g, determined by N_2 isothermal (77K) adsorption (Micrometrics ASAP 2010 BET), as also given in Table 5-1. The fresh and spent catalysts were also characterized by X-ray photoelectron spectroscopy (XPS) using a Kratos Axis Ultra X-ray photoelectron spectrometer, In addition, for some spent catalysts thermogravimetric analysis (TGA) tests were conducted to examine coke deposition on the catalyst in the process of hydro-treatment of the birch-derived bio-crude in supercritical hexane.

5.2.2 Production of bio-crude by hydro-liquefaction of birch powder

The birch wood sample, obtained from a local lumber mill (Northern Wood Ltd), was chipped, milled and screened into fine particles smaller than 20 mesh (~ 0.8 mm). The wood powder was dried in an oven at 105°C in air for 24 hours before use. The proximate and ultimate analysis results (on a dry basis) of the birch sample and the chemical compositions of the ash from the wood sample are given as follows: 78.5 wt% VM, 21.0 wt% FC and 0,5 wt% Ash; 46.9 wt% C, 6.0 wt% H, 0.1 wt% N, 0.1 wt% S and 46.4 wt% O (by difference).

The liquefaction experiments were conducted in a stainless steel autoclave whose details were given elsewhere[35]. The autoclave reactor was heated at about 10°C/min by an external electric heater. The birch powder, the catalyst and the methanol solvent were weighed into the reactor in sequence. In a typical run, 10g of the dried birch powder was weighed into the reactor, followed by adding catalyst in an amount of 5 wt% (w/w) of the woody biomass sample, and then 50g reagent-grade methanol was added. The catalyst used in this work was Rb_2CO_3. The air inside the reactor was displaced with ultrahigh purity hydrogen by repetitive operation of vacuuming and H_2-charging. Then, the reactor was sealed and pressurized to the pre-determined hydrogen pressure (2.0 MPa). The reactor was heated and maintained at 300°C for 60min. After the desired reaction time had elapsed, the electric heater was removed from the reactor, and the reactor was cooled down to ambient temperature quickly with an electric fan and a wet cloth towel. Once the reactor was cooled to room temperature, after releasing the gas, the solid/liquid products were rinsed completely from the reactor with reagent-grade acetone. The resulted suspension was filtered under vacuum through a Whatman No.5 filter paper to recover the solid products (methanol and acetone insoluble). The filtrate was evaporated under reduced pressure at 50°C to remove the solvents (acetone, methanol). After completely removing the solvents, about 50ml ethyl acetate was added to the evaporation flask. The solution was decanted into separatory funnel, followed by the addition of about 50ml distilled water. After 20 minutes the aqueous phase was decanted to the waste liquid bottle. The ethyl acetate solution phase was evaporated under vacuum at a temperature of about 60°C to remove ethyl acetate. The recovered oil after evaporation was used as the bio-crude for the subsequent hydro-treating experiments.

5.2.3 Apparatus and methods for bio-crude hydro-treating

All the hydro-treating tests reported here were carried out in a high-pressure micro-reactor system whose details were given elsewhere[36]. 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, 1g of the bio-crude sample was weighted into the reactor, followed by adding catalyst in an amount of 10 wt% (w/w) of the bio-crude fed, and then 5g of the hexane solvent was added. The solvent/bio-crude ratio was fixed at 5:1 (w/w). The air inside the reactor was displaced with ultra-pure hydrogen by repetitive operation of vacuuming and H_2-charging. Finally, the reactor was pressurized to 2.0~10.0 MPa using H_2, depending on different reaction conditions. Supported on a mechanical shaker (set at 100 rpm), the reactor was then rapidly submerged in a fluidized sand bath pre-heated at the desired temperature for the reaction, i.e., 300-380°C (all above the supercritical conditions of hexane whose critical temperature and pressure is 234.8°C and 3.0 MPa, respectively). After the predetermined reaction time has elapsed, in the range of 30-120 min, the reactor was removed from the sand bath and quenched in a water bath to stop the reactions. Almost all the experimental runs were repeated two times, and the errors in the product yields between the runs under the same conditions were ensured within 5% of the yields. Once the reactor was cooled to room temperature, the gas inside was collected in a gas bag (800 ml). The solid/liquid products were rinsed completely from the reactor with tetrahydrofuran into a beaker. The resulted mixture was filtered through a glass-fiber filter (Ahlstrom 111) to recover catalyst and tetrahydrofuran insolubles. The tetrahydrofuran insolubles were designated as 'Residue'. The resulted filtrate was evaporated at 40°C under reduced pressure in a flask to completely remove the tetrahydrofuran solvent. The liquid after evaporation contained upgraded oil and the water as a HDO product.

The water was removed by absorption employing anhydrous $MgSO_4$ in order to obtain the oil product. Determination of yields of 'Oil' and 'H_2O' has been observed challenging due to the significant oil loss in the processes of both evaporation and $MgSO_4$ absorption. Accordingly, in the present work, oil and water products were lumped as 'Oil +H_2O', and its yield was simply calculated by difference (= 100 wt% - Gas yield – Residue yield).

5.2.4 Analysis of the upgrading products

The compositions of gaseous products were determined using an Agilent 3000 Micro-GC equipped with dual columns (Molecular Sieve and PLOT-Q) and thermal conductivity detectors. The liquid products were analyzed by a gas chromatograph equipped with a mass selective detector [Varian 1200 Quadrupole GC/MS (EI), Varian CP-3800 GC equipped with VF-5 ms column (5% phenyl 95% dimethylpolysiloxane, 30 m×0.25 mm×0.25 μm); temperature program: 40°C (hold 2 min) →190°C (12°C/min) → 290°C (8 °C/min, hold 20 min)]. Compounds in liquid products were identified by means of the NIST 98 MS library with the 2002 update. The elemental compositions (C, H and N) of original bio-crude and the upgraded oil products were determined with a CEC (SCP) 240-XA elemental analyzer. The composition of oxygen (O) was estimated by difference, assuming negligible content of sulfur (S) in the oil products. The liquid products were also analyzed by Fourier Transform Infrared Spectroscopy (FTIR) to examine the change in functional groups, especially the oxygen containing groups like O-H in phenols and C=O in carboxylic acids, aldehydes and ketones, during the treatment.

5.3 Results and Discussion

5.3.1 Influence of the cold pressure of H_2

Fig.5-2 shows the product yields during hydro-treating of the bio-crude at 350°C for a fixed length of reaction time (60 min), while the cold pressure of H_2 was varied at different levels, i.e., 2.0MPa, 5.0 MPa and 10.0 MPa. It is clearly shown in the figure that as the cold pressure of H_2 increased from 2.0MPa to 5.0 MPa, (Oil+H_2O) yield (60%) decreased slightly (54%), while the cold pressure of H_2 continue to increase from 5.0MPa to 10.0 MPa, (Oil+H_2O) yield climbed significantly to 90%, with residue yield declined sharply to 9%. In all the tests, the yields of gaseous products were lower than 5 wt%, and the main gaseous species detected were CO_2, CH_4, CO with very small amounts of C_2 and C_3 hydrocarbon gases. It is well known that the increase of hydrogen pressure can reduce the char yield for hydro-liquefaction of biomass, as observed by the authors' group[37] in hydro-liquefaction of a woody biomass, where higher yields of liquid oil products were obtained with a higher cold pressure of H_2 in the reaction system. High hydeoxygenation (HDO) rates were also achieved by previous researches on hydro-treating bio-oil with a higher cold pressure of H_2. Baldauf and Balfanz[38,39] performed catalytic hydro-treating with both sulfided CoMo and sulfided NiMo catalysts in a continuous-feed bench-scale reactor operated at 17.8 MPa. At weight hourly space velocities of 0.25-0.8 g/(g h) and temperatures of 350-370 °C, high deoxygenation efficiencies of over 90%, and constant product yields of 80-90% for (Oil+H_2O) (30-35% Oil and 50-55% water) and 15- 20% for gases were achieved. Kaiser[40] processed the heavy pyrolysis oil with powdered NiMo catalyst at 30 MPa and 380 °C in a tubular reactor (2 m by 10 cm), and obtained 33.9% yield of highly deoxygenated lightest oil products containing less than 0.1% oxygen. Due to the limitation in the hydrogen source in the present work, tests with a cold hydrogen pressure higher than 10 MPa were not performed, while from the results shown in Figure 5-2 a greater HDO efficiency may reasonably be predicted at a higher hydrogen pressure.

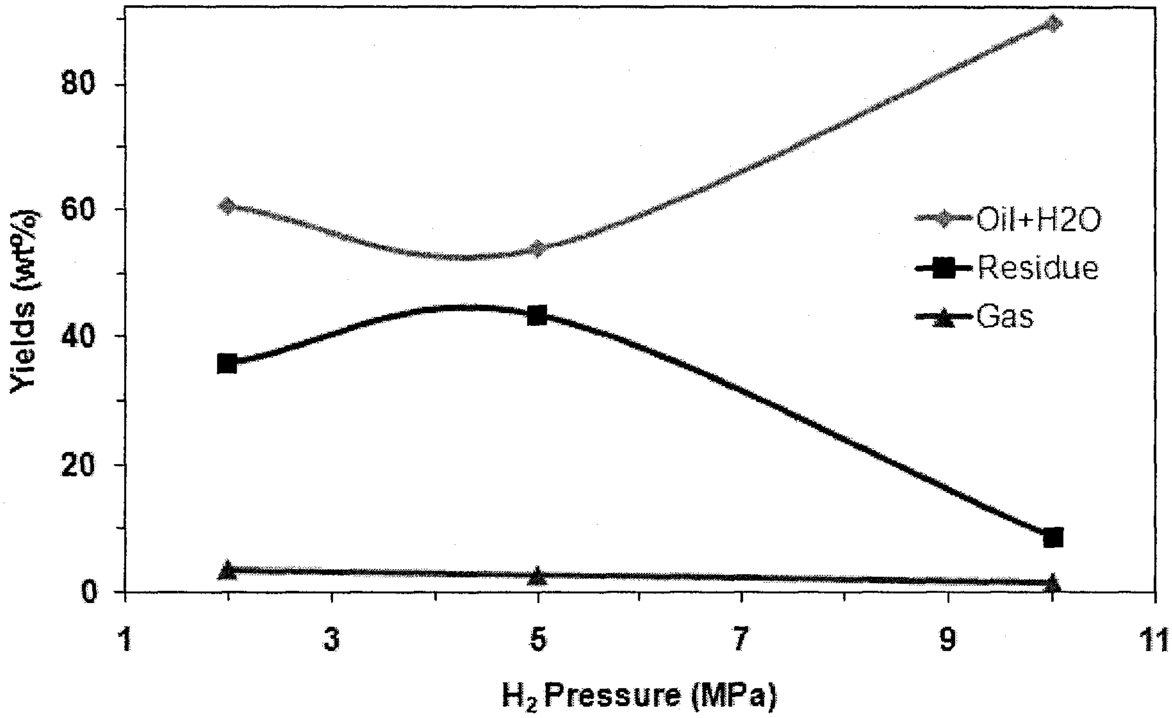

Fig.5-2. Yields of products as function of the cold pressure of H_2 in hydro-treatment of the bio-crude in supercritical hexane for 60 min with CoMoP/MgO catalysts at 350°C.

5.3.2 Influence of residence time

Fig.5-3 shows the yields of bio-crude hydro-treating products at 350°C for different lengths of reaction time ranging from 30 min to 120 min with a cold pressure of H_2 at 5 MPa. Being similar to the observation for the effects of the cold pressure of hydrogen as discussed above: the yield of (Oil+H_2O) decreased slightly with residence time up to 60 min, but increased remarkably as the residence time was prolonged to 120 min, accompanied by a opposite trend for the residue yield. For instance, the yields of (Oil+H_2O) declined slightly from 59% to 54% as the reaction time increased from 30 min to 60 min, and it climbed significantly from 54% to about 75% upon increasing the residence time from 60 min to 120 min. Meanwhile, the THF-insoluble residue yields increased from 40% for 30 min, to 43% for 60 min, but declined markedly to 23% for 120 min. As expected, the gas formation increased monotonically with increasing residence time, but the gas yields were all below 5%. As such, it may be concluded that longer residence time is a favorable condition for producing upgraded bio-crude in supercritical hexane. The above observations however differ from a previous work on hydro-treating of pyrolysis oil in tetralin with CoMoP/γ-Al_2O_3 catalyst[18], where a declining oil yield and a climbing char yield was observed with increasing residence time after 45 min due to "coking" of the heavy oil products to form char/coke by condensation and dehydration reactions. The above comparison might suggest that supercritical hexane and the MgO supported catalyst could be advantageous reaction medium and catalyst with respect to their superior performance in preventing condensation of the heavy oil products to form coke/char. The above superior performance of a supercritical hexane is likely due to the fact that hexane at supercritical states possesses an excellent diffusivity for hydrogen gas and a greatly increased solubility for the liquid intermediates/products derived from hydrodeoxygenation of bio-crudes, both leading to retardance of the condensation reactions to form residue/coke. Furthermore, as stated by Klicpera and Zdrazil[26], the basic character of the support (MgO) could also inhibit coking which is rather intensive over the conventional Al_2O_3-supported catalysts.

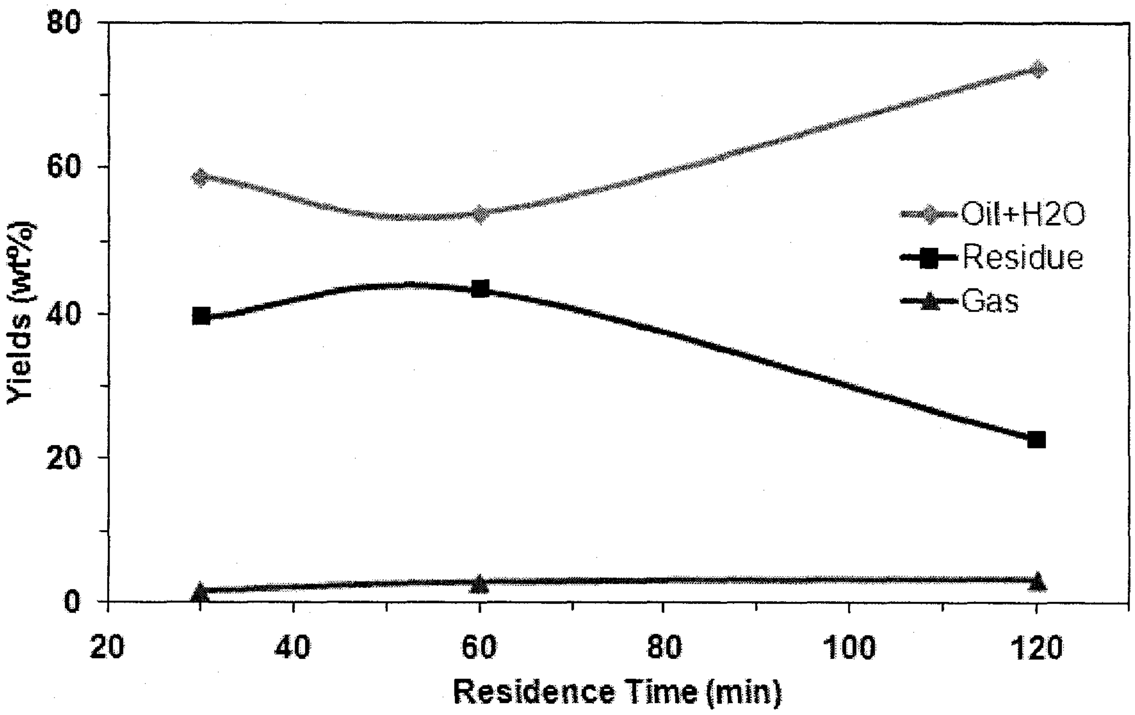

Fig.5-3.Yields of products as function of residence time in hydro-treatment of the bio-crude in supercritical hexane under H_2 of a cold pressure of 5.0 MPa with CoMoP/MgO catalysts at 350°C.

5.3.3 Effect of treatment temperature

The effects of treatment temperature on the product yields in hydro-treating the bio-crude are shown in Fig.5-4, where the results were obtained from the experimental runs at various temperatures of 300°C, 350°C to 380°C, while under the same remaining conditions (5.0 MPa H_2, solvent-to-bio-crude ratio of 5/1, residence time of 60 min, and with CoMoP/MgO catalyst). As clearly shown from the figure, the operation temperature significantly affected the bio-crude hydro-treating process in supercritical hexane: the gas yield increased continuously as the temperature increased from 300°C to 380°C, with 0.5 wt% at 300°C climbing to 4 wt% at 380°C. Over the tested temperature range (300-380°C), the yields of liquid products decreased with increasing temperature, to the minimum yield of 54 wt% (Oil+H_2O) at about 350°C. As the operation temperature further increased to 380°C, the (Oil+H_2O) yield increased to 64 wt%, accompanied by a drastic decrease in char yield from 43 % at 350°C to 30 wt% at 380°C. It might suggest that a higher temperature is preferable to achieve a better HDO efficiency for hyrdo-treating the bio-crude. Similar experiment results were obtained by Zhang et al.[18] in upgrading of fast pyrolysis bio-oil with CoMoP/γ-Al_2O_3 catalyst. Their study demonstrated that at a lower temperature (around 345°C), conversion and oil yield both were very low, but increased rapidly with reaction temperature, whereas no further significant change in the product yields was observed when the reaction temperature surpassed a certain value (at around 380°C). Gevert and Otterstedt[41] performed catalytic hydro-processing tests using the decalin–extracted bio-oil with sulfided CoMo/γ-Al_2O_3 catalyst. It was found that coke deposition on the catalyst was at a minimum at around 350-375°C, but increased as the operating temperature climbed up further. The above results with the conventional sulfided CoMo/γ-Al_2O_3 catalyst apparently differ from our findings as shown in Figure 5-4, in that a maximum residue was shown at around 350°C, but the residue yield reduced greatly at a higher temperature, suggesting that more of the heavier components in the feed were converted to hydro-deoxygenated lighter components at a higher temperature. The superior performance (with very little coke formation) of the present system of supercritical hexane with sulfided CoMoP/MgO in HDO of bio-oil might be related with the excellent diffusivity for hydrogen gas in supercritical medium, which could stabilize the coke precursors and preventing from their condensation reactions to form coke. Moreover, the basic character of the support (MgO) could also inhibit coking which is rather intensive over the conventional Al_2O_3-supported catalysts[26]. In addition, adsorption and desorption of the reactants and products on the catalyst's may be taken into account. The superior performance of the present system of supercritical hexane with sulfided CoMoP/MgO might facilitate desorption of the reaction products, leading to a decrease in the average residence time of the coke precursor molecules on the catalyst surface at a temperature above 350°C. This would retard unwanted side-reactions on the catalyst surface and thus reduce coke formation.

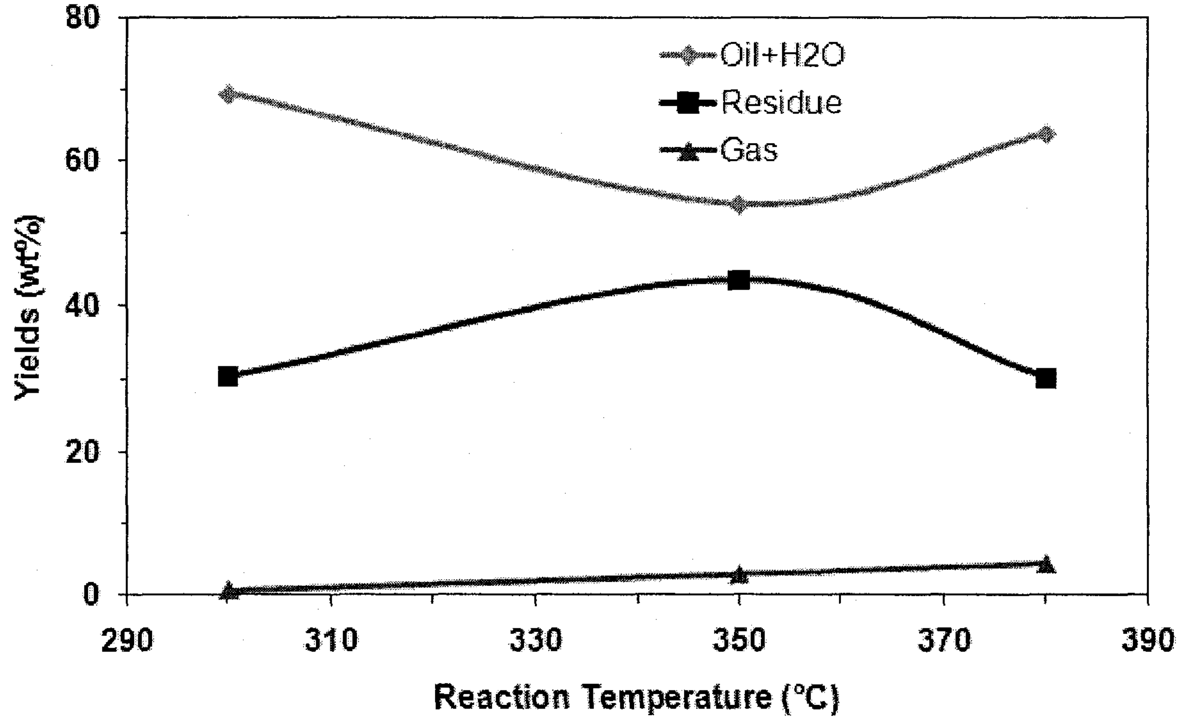

Fig.5-4. Yields of products as function of reaction temperature in hydro-treatment of the bio-crude in supercritical hexane under H_2 of a cold pressure of 5.0 MPa for 60 min with CoMoP/MgO catalysts.

5.3.4 Characterizations of the hydro-treated oil products

Properties of the hydro-treated oil products are of a particular interest in this work. The elemental compositions (C, H, N, O) of some typical hydro-treated oil products are presented in Table 5-2, where the elemental compositions of the un-treated bio-crude are also provided for comparison. The oxygen contents of the samples were obtained by difference assuming negligible sulfur content (true for wood-derived bio-oil). Compared with the original bio-crude, all hydro-treated oil products have increased contents of carbon and hydrogen, and reduced concentrations of oxygen and nitrogen, as a result of the HDO reactions, leading to increased calorific values of the hydro-treated oils. For instance, the hydro-treatment at 350°C for 60 min under hydrogen of a cold pressure at 5 MPa produced an upgraded oil product with an oxygen content of 16.1% in relation to 26.2% for the un-treated original bio-crude, and an HHV of 34 MJ/kg compared with 27 MJ/kg for the un-treated bio-crude. The higher heating values listed in the Table were calculated based on the widely accepted Dulong Formula (HHV (MJ/kg) = 0.3383C + 1.422 (H – O/8)). All the hydro-treated oil products contain a greater HHV than that of the un-treated bio-crude, as clearly shown in the Table. The quality of the oil products was found to be strongly dependent on the treatment conditions: temperature, time and hydrogen pressure. As a general conclusion, the quality of the treated oil increased with increasing temperature, residence time and cold pressure of hydrogen in the hydro-treating operations. The elemental analysis results of the oil products also suggest the occurrence of hydrogenation reactions and hydrodenitrogenation (HDN) reactions, implied by the significantly increased H/C molar ratio and the greatly reduced nitrogen contents in the treated oils. For example, the hydro-treatment at 350°C for 60 min with 5 MPa of hydrogen produced an upgraded oil product of an H/C ratio of 1.25, and a nitrogen content of 0.18%, compared to an H/C of 1.16 and 0.61% N for the un-treated bio-crude. The HDN efficiency was the highest at 380°C, leading to an oil product with only 0.05% N. In accordance with previous researchers by Furimsky[42,43] for hydro-treating heavy gas oil at 400°C with a sulfided $CoMo/Al_2O_3$ catalyst under 13.7 MPa H_2, the catalyst showed the following order of relative effectiveness for the removal of heteroatoms (S, N, O): hydrodesulphurization (HDS) > hydrodenitrogenation (HDN) > Hydrodeoxygenation (HDO). It was suggested that that the much greater bonding strength of the aromatic-OH bonds (predominant in the wood-derived bio-oils) than the aromatic/or aliphatic–NH_2 bonds could account for the catalyst's lower activity towards HDO than that for HDN.

Table 5-2 Elemental compositions of the un-treated bio-crude and the hydro-treated oil products from the bio-crude in supercritical hexane with CoMoP/MgO.

Sample	Elemental compositions, wt% (d.b.)$^{(1)}$ C	H	N	O$^{(2)}$	H/C	HHV$^{(6)}$ (MJ/kg)
Un-treated bio-oil	66.72	6.47	0.61	26.20	1.16	27.1
Treated oil, 300°C$^{(3)}$	69.98	6.31	0.41	23.30	1.08	28.5
Treated oil, 380°C$^{(3)}$	74.31	7.61	0.05	18.03	1.23	32.8
Treated oil, 30 min$^{(4)}$	73.31	7.38	0.21	19.10	1.21	31.9
Treated oil, 120 min$^{(4)}$	75.42	7.61	0.16	16.81	1.21	33.3
Treated oil, 2 MPa$^{(5)}$	67.98	6.97	0.27	24.78	1.23	28.5
Treated oil, 5 MPa$^{(5)}$	75.81	7.88	0.18	16.13	1.25	34.0
Treated oil, 10 MPa$^{(5)}$	73.14	7.34	0.29	19.23	1.20	31.8

[1] On a dry basis;

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

[3] Under the same remaining reaction conditions: 5.0 MPa H_2, residence time of 60 min;

[4] Under the same remaining reaction conditions: 5.0 MPa H_2, 350°C;

[5] Under the same remaining reaction conditions: 350°C, 60min;

[6] Higher heating value (HHV) by the Dulong Formula: HHV (MJ/kg) = 0.3383C + 1.422 (H – O/8).

Table 5-3 shows the volatile compounds (determined by GC/MS analysis) in the un-treated bio-crude and the upgraded oil products from the hydro-treatment of the bio-crude in supercritical hexane under 5.0 MPa H_2 for 60 min at various temperatures with CoMoP/MgO catalyst. The area % for each compound identified (defined by percentage of the compound's chromatographic area out of the total area) and the total area % for the major compounds identified are shown in the Table. The un-treated bio-crude, as expected, contains significant amounts of phenolic and derivative compounds (>50%), carboxylic acids/esters (~25%), a very small amount of ketones (<5%), and almost free of alkanes and alkenes. It can be seen from the Table that very high proportions of phenol derivatives and acids/esters, such as 2,4-dimethoxyphenol (8.8%), 2,4,6-Trimethoxytoluene (6.1%), 2,6-dimethoxy-4-(2-propenyl)-phenol (4.3%), and dimethyl ester nonanedioic acid (5.5%) were observed in the un-treated bio-crude. As well known, the phenolic compounds were originated from the degradation of the lignin component in the lignocellulosic biomass feedstock[35]. As an apparent observation, the relative concentrations of phenol derivative compounds and carboxylic acids/esters dropped due to the hydro-treatment, accompanied by significantly increases in the relative contents of oxygen-lean/free compounds, such as ketones, alcohols and alkanesand alkenes, suggesting HDO effects of the treatment. For example, the hydro-treatment at 380°C resulted in a oil product containing reduced concentrations phenolic and derivative compounds (6.5%) and carboxylic acids/esters (17%), but high concentrations of ketones and alcohols (32%) and alkanes and alkenes (>30%). It can also be seen from Table 5-3 that the relative contents of de-oxygenated products such as hydrocarbons in the upgraded oil products increased significantly with the increase in the reaction temperature. At 300°C, very small amount of HCs (mainly 3,4-diethyl-1,1'-biphenyl) was observed in the oil product. While the reaction temperature increased to 350°C, much more hydrocarbon products were produced, with 2-methyl-1-pentene (13.49%), 1-pentyl-cyclohexene (5.57%), triacontane (4.6%), 3,4-diethyl-1,1'-biphenyl (3.32%) and 1-methylcycloheptene (1.94%). As the reaction temperature increased to 380°C, the total concentration of hydrocarbons increased to more than 30%, with the dominant HC species of 1-methylcycloheptene (9.13%), cyclohexane (8.57%), 3,3-dimethyl-cyclobutene (7.91%) and 5,5-dimethyl-1,3-hexadiene (3.36%). The above changes in organic compounds of upgraded oil products showed that the HDO process employing supercritical hexane and CoMoP/MgO catalyst was effective especially at temperatures > 350°C. As bio-crude is so complex in compositions, the detailed reaction routes in the hydro-treatment are still not fully understood [44]. To this end, more research using model compounds would be needed.

Table 5-3 GC/MS analysis results for the un-treated bio-crude and the hydro-treated oil products obtained in hydro-treatment of bio-crude in supercritical hexane under H_2 of a cold pressure of 5.0 MPa for 60 min at different temperatures with CoMoP/MgO catalysts.

RT (min)	Compound Name	Area %			
		Original Bio-crude	300°C	350°C	380°C
3.431	Cyclobutene, 3,3-dimethyl-				7.91
3.607	Cyclohexane				8.57
3.613	1-pentene, 2-methyl-			13.49	
4.935	2-hexanone, 4-hydroxy-5-methyl-		6.2	10.98	0.99
5.264	5,5-Dimethyl-1,3-hexadiene				3.36
5.504	Butanoic acid, 3,3-dimethyl-	2.36	1.08		
6.184	Hexane, 3-methoxy-	1.37			
6.789	3-hepten-1-ol		2.42	5.74	5.43
6.966	Butanoic acid, 4-hydroxy-		2.84		8.17
8.511	Propanoic acid, 2-methyl-, methyl ester	1.74	2.37		
8.774	Benzene, 1-methoxy-3-methyl-		1.02		2.94
8.894	Butanedioic acid, dimethyl ester	1.67	1.62		
9.06	1-Methylcycloheptene		1.2	1.94	9.13
9.328	2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	1.3			
9.448	Butanedioic acid, methyl-, dimethyl ester	1.21	2.73		4.4
9.876	Phenol, 2-methoxy-	2.62	4.21	5.57	11.27
10.727	Benzene, 1,2-dimethoxy-		1.12	3.45	
11.492	Phenol, 4-methoxy-3-methyl-		1.44		
12.236	Phenol, 2,6-dimethoxy-	1.44	1.68		
12.533	1,2-Benzenediol, 3-methoxy-	1.5			
12.736	Phenol, 4-ethyl-2-methoxy-	2.54	3.81	4.32	
13.153	1,2,3-Trimethoxybenzene	2.94	3.68	2.44	
13.307	Benzene, 4-ethyl-1,2-dimethoxy-	1.13	0.98	1.26	
13.73	phenol, 2,6-dimethoxy-			2.54	1.82
13.759	2,4-Dimethoxyphenol	8.79	10.34		
13.976	Phenol, 2-methoxy-4-propyl-		2.16	4.38	

14.378	Benzene, 1,2,3-trimethoxy-5-methyl-	1.05	1.22	2.41	
14.978	1,2,4-Trimethoxybenzene	2.57		3.59	
15.046	Phenol, 2-methoxy-4-(1-propenyl)-	1.65			
15.826	Benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl-	1.72			
15.945	5-tert-butylpyrogallol	6.07	5.66	6.04	2.75
16.174	Nonanedioic acid, dimethyl ester	5.54	5.16	3.41	2.72
16.346	1,1'-Biphenyl, 3,4-diethyl-	1.28	0.99	3.32	
16.738	Benzoic acid, 3,4-dimethoxy-, methyl ester	1.38			
16.894	Phenol, 2,6-dimethoxy-4-(2-propenyl)-	4.3	1.14		
16.937	Benzene, 1,1'-propylidenebis-			4.95	1.75
16.98	2,4-Dimethoxybenzyl alcohol	3.45	5.59		
17.634	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	2.22			
17.871	Ethanone, 1-(3,4,5-trimethoxyphenyl)-	2.02	0.97		
18.443	Benzoic acid, 3,4,5-trimethoxy-, methyl ester	1.95	0.93		
18.696	Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	2.98			
19.301	3,4,5- Trimethoxybenzyl methyl ether	2.85			
22.681	Hexadecanoic acid, methyl ester	2.93	2.75	1.66	7.12
28.168	Octadecanoic acid, methyl ester	2.67	2.7	1.81	7.17
31.101	Eicosanoic acid, methyl ester	1.83	1.75	1.76	
33.598	Dotriacontane			4.6	
Total		79.1	81.0	89.1	85.2

Fig.5-5 shows the FTIR spectra of the un-treated bio-crude and the hydro-treated oil products at various reaction temperatures (300°C, 350°C and 380°C) with CoMoP/MgO catalyst. The presence of alkanes may be indicated by the C–H stretching vibrations between 3000 and 2800 cm^{-1}, as well as the C–H deformation vibrations between 1490 and 1350 cm^{-1}, according to Li et al.[45]. The increase in peak intensity between 3000 and 2800 cm^{-1} for the hydro-treated oils may suggest increased concentrations of alkanes in the upgraded oils, compared with that of the un-treated bio-crude, as evidenced by the GC/MS analysis results in Table 5-3. The FTIR spectra of the upgraded oil products differ greatly from that of the un-treated bio-crude in the region of 1700–1000 cm^{-1}. The bands between 1700 and 1650 cm^{-1} may be attributed to the stretching vibrations of C=O group which indicate the presence of organic acid, ketone and aldehyde groups. The weakening of the peak at around 1700 cm^{-1} for the hydro-treated oils, as shown in

Figure, suggests partial removal of the oxygen-containing compounds of carboxylic acids and ketones and aldehydes in bio-crude, being in a good agreement with the GC/MS analysis results discussed previously. In addition, the markedly decreasing peak intensity between 1300 and 1000 cm^{-1} indicates weakening of C–O stretching and O–H deformation vibrations of phenols, acids and alcohols in the upgraded oil products, which suggests partial removal of the phenolic and acid compounds through the HDO process.

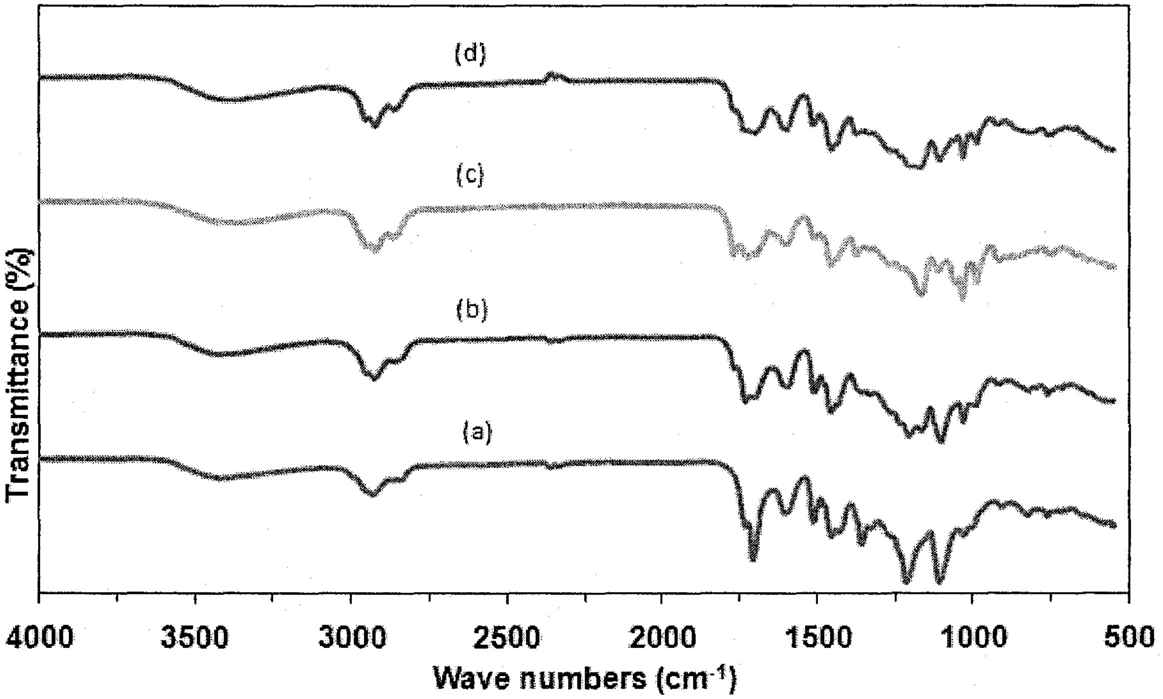

Fig.5-5. FTIR spectra of the un-treated bio-crude (a) and the upgraded oil products in supercritical hexane for 60 min with CoMoP/MgO catalyst at 300°C (b), 350°C (c) and 380°C (d).

5.3.5 Characterizations of the fresh and spent catalysts

The fresh and spent catalysts of CoMoP/MgO (after the hydro-treatment at 300, 350 and 380 °C for 60 min and 5 MPa H_2) were characterized with a Kratos Axis Ultra X-ray photoelectron spectrometer. The XPS spectra were obtained from an area of approximately 300 x 700 microns using a pass-energy of 160 eV. According to the S 2p spectra (for either the fresh or spent catalyst), sulphur exists in the states of primarily S^{2-} (S 2p peak at around 160 ± 0.5 eV) resulting from the formation of MoS_2 during the sulfidation operation with H_2S[46,47]. Another relatively weak S 2p peak at around 167 ± 0.5 eV observed in all samples may be ascribable to the sulfate species that could be formed by air oxidation of sample prior to or during the XPS measurements. From the XPS spectra of Co 2p for the fresh and spent catalysts of CoMoP/MgO ,very weak Co $2p_{3/2}$ peak of binding energy at 778.6 eV were detected in the fresh CoMoP/MgO catalyst. Previous work by Alstrup et al.[48] showed that treatment of the $Co/SiO_2/Si(100)$ model catalyst in a mixture of H_2S and H_2 at room temperature or a higher temperature could completely convert the cobalt in the sulfidic state, evidenced by the Co $2p_{3/2}$ binding energy of 778.2 to 778.6 eV. Even at room temperature, exposure of well dispersed cobalt oxide to H_2S would result in complete conversion of CoO to CoS[49]. In the present study, the calcinated CoMo/MgO and CoMoP/MgO catalysts were sulfided in a flow of $5\%H_2S/H_2$ at 400°C for 4 hours, which shall lead to complete conversion of Co to CoS, but it is possible that a small amount of Co may still exist in oxide state. Fig. 5-6 illustrates the XPS spectra of Mo 3d for the fresh and spent catalysts of CoMoP/MgO. The Mo 3d spectrum of the fresh CoMoP/MgO consists of a doublet with binding energy between 228-234 eV. The shoulder peak at 232.6 ev is characteristic of Mo^{6+} in MoO_3[50,51], and the main peak with binding energy of 229.0 eV may be ascribed to Mo^{4+} in MoS_2[52-55]. After treatment at different temperatures, both the Co $2p_{3/2}$ peak and Mo 3d peaks almost disappeared. This might result from the coke deposition on the catalyst surface, which would shield Co $2p_{3/2}$ and Mo 3d peaks from being effectively detected.

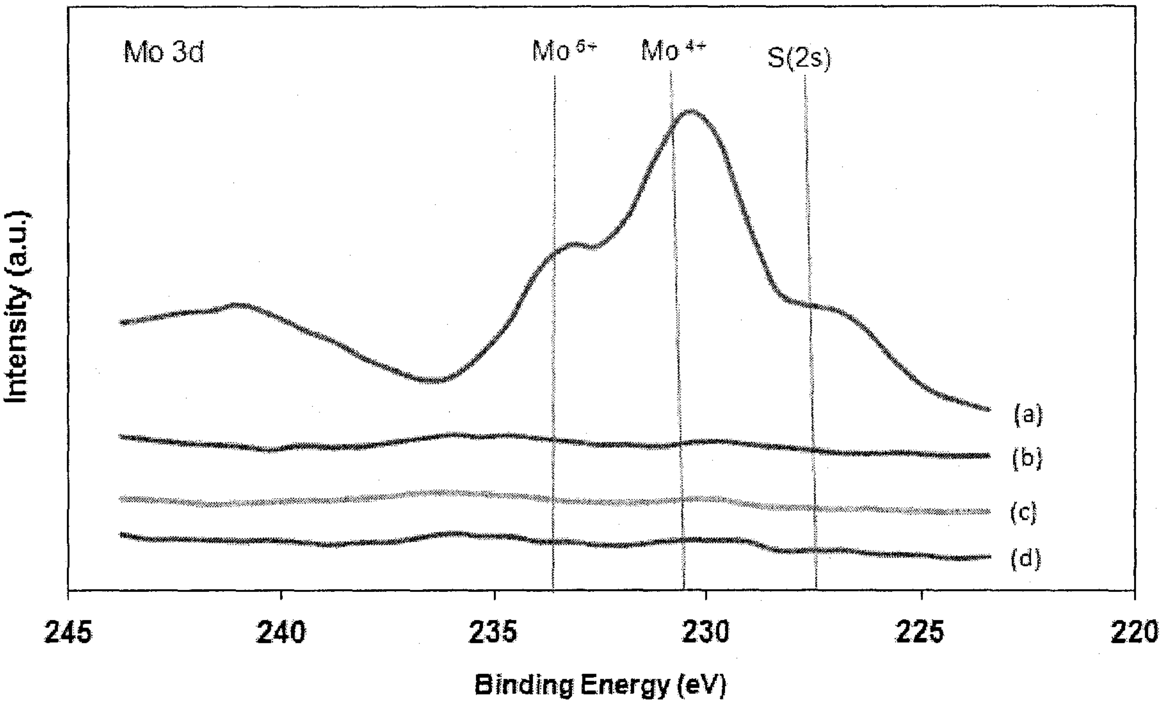

Fig.5-6. Mo 3d XPS spectra for the fresh CoMoP/MgO catalyst (a), and the spent catalyst after treatment at 380°C(b), 350°C (c) and 300°C (d).

In order to examine the extent of coke formation during hydro-treatment of the bio-crude with CoMoP/MgO catalyst, TGA measurements were employed for the spent catalysts. The TGA profiles of the spent catalysts after hydro-treatment of the bio-crude in supercritical hexane under H_2 of a cold pressure of 5.0 MPa for 60 min at 300, 350 and 380 °C are illustrated in Fig. 5-7. The TGA profiles were collected for the spent catalysts heated at 10 K/min from room temperature up to 900°C in 30 ml/min flow of air. The weight loss up to 200°C (of 5.3 wt%, 4.7 wt% and 3.7 wt% for the 300, 350 and 380 °C samples, respectively) may be attributed to the removal of the water and lighter organics in the catalysts. The weight loss between 250 and 600°C may be attributed to the combustion of heavier residual coke and tar deposited on the catalysts. If evaluating the coke deposition by the weight loss between 250 and 600°C, the deposited amounts of coke in the spent catalysts of the treatment at 300, 350 and 380 °C were 63 wt%, 66 wt% and 60%, respectively. This result may suggest a lower coke deposition for the catalyst at 380°C, or more of the heavier components in the bio-crude being upgraded converted to lighter components, which is in a good agreement with the results of product yields (Figure 5-4), up-graded oil compositions (Table 5-3), as discussed previously.

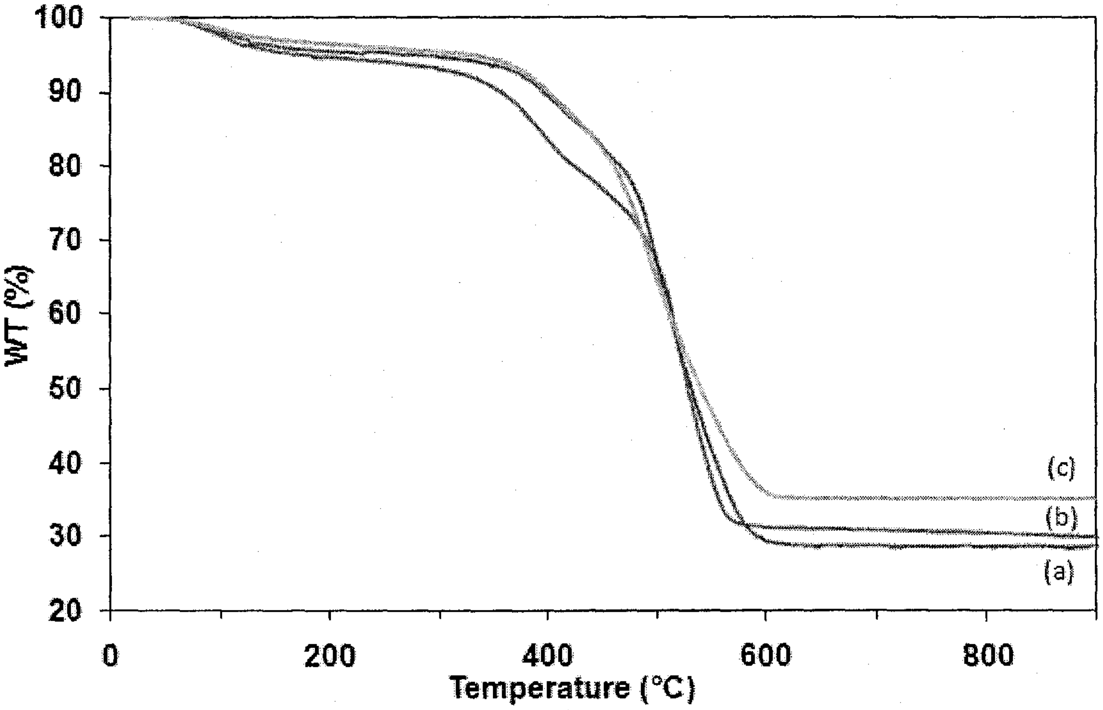

Fig.5-7.TGA profiles of the spent catalysts of CoMoP/MgO after hydro-treatment of the bio-crude in supercritical hexane under H_2 of a cold pressure of 5.0 MPa for 60 min at different temperatures: 300°C(a), 350°C(b) and 380°C(c).

5.4 Conclusions

In this study, hydrodeoxygenation (HDO) of bio-crude from direct liquefaction of birch powder was investigated in supercritical hexane at temperatures of 300-380°C with hydrogen of a cold pressure of 2.0-10.0 MPa and a MgO-supported sulfided CoMo with phosphorus as the catalyst promoter. The sulfided CoMoP/MgO catalyst proved to be effective for HDO of the bio-crude in supercritical hexane at 350°C and above, and its effectiveness increased at 380°C. Revealed by elemental analysis (C, H and N) for the hydro-treated oils, the treatment resulted in a remarkably high removal of nitrogen (>90%), suggesting that CoMoP/MgO is a highly active catalyst for the HDN of the bio-oil. The GC/MS results for the upgraded oils at 350°C and 380°C demonstrated that the effective conversions of phneolic compounds and acids/esters into oxygen-lean/free compounds such as ketone/alcohol and hydrocarbons during the hydro-treatment. The supercritical hexane upgrading process proved to be an effective and promising way to upgrade bio-crude, which can be an alternative process for the conventional ones involving expensive and unrecyclable hydro-treating solvents such as tetralin.

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CHAPTER 6

Conclusions and Recommended Future Work

6.1. Summary and Conclusions

This thesis conducted research in the convert of forest biomass (birch powder) into valuable bio-fuels through hydro-liquefaction (high-pressure direct liquefaction under hydrogen atmosphere) for bio-crudes and upgrading bio-crudes by catalytic hydrodeoxygenation (HDO). The HDO of phenol as a model compound for bio-crude was also investigated. High yields of heavy oil (>30 wt%) of a HHV > 30 MJ/kg were obtained by hydro-liquefaction of birch powder in sub-/super-critical methanol. Moreover, for the first time, the novel MgO-supported sulfided CoMo and CoMoP catalysts were used to upgrading bio-oil in super-critical hexane. Revealed by GC/MS, FT-IR and CHN analysis, high HDO rate was achieved and the quality of upgraded oil was significantly improved. The detailed conclusions for each part of this work are summarized as follows.

Part-I: Hydro-liquefaction of birch powder in supercritical methanol

(1) Longer residence time and a lower initial H_2 pressure were found to be favorable conditions for the producing heavy oil products from biomass in sub-/supercritical methanol, while the optimal temperature for the heavy oil production appeared to be at around 350°C.

(2) The addition of a basic catalyst of NaOH, K_2CO_3 or Rb_2CO_3 not only significantly enhanced biomass conversion or suppressed char formation, but also greatly

increased the yields of liquid and gas products, in particular when the operation temperature was lower than 300°C. Compared with NaOH, K_2CO_3 and Rb_2CO_3 showed higher catalytic activities. The yield of heavy oil attained about 30 wt% for the liquefaction operation in the presence of 5 wt% K_2CO_3 or Rb_2CO_3 at 300°C and 2 MPa of H_2 for 60 min.

(3) Revealed by the GC-MS measurements, phenol derivatives, esters and benzene derivatives were the dominant compounds detected in the obtained heavy oil products, while their compositions could be altered by catalysts.

(4) The HO products from the operations have a HHV of above 30 MJ/kg in relation to only 16 MJ/kg for the crude birch wood. Hydro-liquefaction in methanol can thus be a promising technique for upgrading of woodwastes of a low-heating value to bio-crude with a significantly increased heating value.

Part-II: HDO of phenol as a model compound for bio-crude in supercritical hexane.

(1) Both MgO-supported catalysts proved to be effective for HDO of phenol in supercritical hexane at >350°C. The HDO activity of the catalyst was greatly promoted by addition of a small amount of phosphorus.

(2) The HDO of phenol may proceed with direct hydrogenolysis reaction and hydrogenation reaction involving cyclohexanol as an intermediate/precursor, resulting in conversion of phenol into benzene, cyclohexyl-aromatics and C_{12}-products.

Hydrogenolysis of phenol to benzene (direct elimination of the hydroxyl group) is the dominant reaction and it becomes much more favorable at a higher temperature.

(3) The HDO activity of CoMoP/MgO increased drastically with increasing the reaction temperature. The hydro-treatment of phenol at 450°C with CoMoP/MgO catalyst led to a liquid product containing 10.2% phenol and 64% benzene.

(4) The superior resistance to coke deposition for the MgO-supported catalysts may be related with the basic character of the MgO support, and the presence of a small amount of phosphorus in the CoMo/MgO catalyst could further enhance the catalyst's resistance to coking.

Part-III: HDO of bio-crude produced from hydro-liquefaction of birch powder.

(1) The sulfided CoMoP/MgO catalyst proved to be effective for HDO of the bio-crude in supercritical hexane at 350°C and above, and its effectiveness increased at 380°C.

(2) Revealed by elemental analysis (C, H and N) for the hydro-treated oils, the treatment resulted in a remarkably high removal of nitrogen (>90%), suggesting that CoMoP/MgO is a highly active catalyst for the HDN of the bio-oil.

(3) The GC/MS results for the upgraded oils at 350°C and 380°C demonstrated that the effective conversions of phneolic compounds and acids/esters into oxygen-lean/free compounds such as ketone/alcohol and hydrocarbons during the hydro-treatment.

(4) The supercritical hexane upgrading process proved to be an effective and promising way to upgrade bio-crude, which can be an alternative process for the conventional ones involving expensive and unrecyclable hydro-treating solvents such as tetralin.

6.2. Recommendations for Future Work

This thesis work involved bench-scale exploration tests for hydro-liquefaction of birch powder in supercritical methanol for the production of bio-crude, and hydrodeoxygenation (HDO) of phenol and bio-crude in supercritical hexane with novel MgO supported CoMo and CoMoP catalysts. 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 hydro-liquefaction, the following recommendations may be considered for future research:

- Based on the present experimental results and literature, it is possible to produce higher yield of heavy oil by optimizing the experimental parameters such as using better catalysts.
- The liquid products separation procedure for heavy oil recovery (presently by evaporation) may be improved by using solvent (like ethyl actate) extraction, or simply by phase separation naturally for better energy efficiency.

For upgrading of bio-crude by hydrodeoxygenation (HDO), the following recommendations may be useful:

- Generally, the surface areas of the MgO supported CoMo and CoMoP catalysts are relatively low because MgO reacts easily with H_2O to form $Mg(OH)_2$ during aqueous impregnation. Organic solvents such as dimethylsulfoxide (DMSO) and methanol (ethanol), may be used in the future work when preparing MgO supported catalysts with the successive incipient wetness impregnation method.
- The present bio-crude HDO experiments were mainly conducted in low temperature range (300-380°C), although relatively high catalytic activities were achieved, higher reaction temperatures above 400°C may be employed in future study to examine the catalytic activities.
- A continuous flow-type reactor may be utilized in future work for upgrading bio-crudes by hydro-treating.
- The anti-deactivation ability of MgO supported CoMoP catalyst will be examined with longer reaction time and reuse of the catalyst.
- The roles of the MgO-supported catalysts in HDO of bio-crude (complex mixture phenols, ketones, acids and aldehydes) should be further investigated.