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Low-Temperature Hydrothermal Liquefaction of Giant Miscanthus with Alcohol as Cosolvent

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Low-temperature hydrothermal liquefaction of giant miscanthus with alcohol as co-
solvent

By

Islam Hassan Hafez

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Master of Science
in Forest Products
in the Department of Forest Products

Mississippi State, Mississippi

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2012

Low-temperature hydrothermal liquefaction of giant miscanthus with alcohol as co-
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Energy issues in the United States are currently receiving a very high priority. There is a strong desire to replace fossil fuels with alternative sources of energy since fuel prices are rising dramatically, and for the harming effect on the environment. Biomass is one of the most promising alternative sources of energy. In this study, hydrothermal liquefaction with alcohol co-solvents was applied on giant miscanthus (*Miscanthus giganteus*) feedstock. All liquefaction experiments were conducted in 5500 series Parr[®] reactor. The most important parameters that affect the liquefaction process were studied. The yield of the liquefaction process was determined gravimetrically and the produced bio-oils were characterized. Bio-oil obtained at the optimum conditions was upgraded using different solid acid catalysts and the chemical composition for the upgraded bio-oil was determined. In a new study, the solid acids were added directly during the liquefaction process to produce upgraded bio-oil in one liquefaction/upgrading step.

Keywords: biomass, hydrothermal liquefaction, alcohols, fuels

DEDICATION

I would like to dedicate this thesis to my lovely family.

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CHAPTER I

INTRODUCTION

Energy issues in the United States are currently receiving a very high priority. There is a strong desire for alternative sources of energy since fuels prices are increasing dramatically. The price of crude barrel oil has more than tripled since 2003; it increased from around \$30 to over \$90 today. Also, the environmental and health impacts associated with fossil fuels necessitate seeking of new renewable energy sources (Balke et al, 2008).

Biomass, the fourth largest energy source worldwide, has always been a major and important source of energy for humanity; it is estimated to contribute to 10-14% of the world's energy supply (McKendry, 2002). Basically, biomass composes of natural polymers; cellulose (40-50%), hemicellulose (20-30%), and lignin (20-30%) (Panshin, 1980). Cellulose is the most abundant on earth; it composes of highly crystalline homopolymer of D-glucose, with a degree of polymerization of up to 10000 or higher. Hemicelluloses are complex heterogeneous polysaccharides composed of D-glucose, D-galactose, D-mannose, D-xylose, and L-arabinose. Lignin is a branched, complex polymer and the most abundant non-carbohydrate constituent of biomass, it glues the cellulose and hemicelluloses together to provide strength and stiffness (Willför et al., 2005a; Willför et al., 2005b).

The southeast of the United States and many other parts of the Midwest are ideal regions for the production of high yield perennial grasses. Giant miscanthus (*Miscanthus giganteus*) is one of the best perennial grasses grown in the southern parts of US when compared to other biomass due to numerous of advantages. It can yield up to 15 tons/acre/year and a height of up to 15 ft (Bassam, 2010).

There are many conversion technologies by which the biomass can be converted into other forms of energy; the three main methods are thermochemical, chemical, and biochemical. Thermochemical conversion technologies can be divided in turn into four methods; combustion, pyrolysis, gasification and direct liquefaction. Combustion is one of the oldest conversion methods used in the conversion of biomass into heat with low efficiency compared to the other methods. Pyrolysis is a thermochemical decomposition of organic material at elevated temperatures in the absence of oxygen. Gasification is the process that converts the biomass into synthesis gas or syngas (carbon monoxide, hydrogen and carbon dioxide) at elevated temperatures under a controlled amount of oxygen (Demirbas, 2000).

In the last few decades, hydrothermal liquefaction of biomass had gained an increased importance - with the starting of oil crisis in the 1970s - as an environmentally friendly process because water is the most ecologically benign solvent that can be used for industrial applications. Hydrothermal liquefaction-only water is used- had been studied and used for many years, however, high temperatures and pressures are to be held at or below the critical temperature of water 374 °C, resulting in a pressure of 2500–3000 psi to successfully run the process. At these conditions, water has a range of exotic properties, for example, it is a poor solvent for electrolytes, however, it is a very good

solvent for non-polar molecules, due to its low dielectric constant and poor hydrogen bonding. Viscosity and dielectric both decrease at this point. For these reasons, water is an important reactant and catalyst, and thus the biomass can be directly converted without an energy consuming drying step, as in the case of pyrolysis (Bridgwater et al., 1999). The addition of ethanol to water system showed a synergistic effect on biomass conversion process and it decreases the energy inputs such as the temperature required for the reaction, which in turns decreases the total costs of the process since the critical point of water-ethanol system was decreased and lower temperature is needed. Moreover, the solvent could be easily recycled by evaporation after the process and reused (Cheng et al., 2010).

CHAPTER II

LITERATURE REVIEW

2.1 Biomass resources

There is a wide range of biomass feedstocks. They include crops specifically grown for bioenergy, and various agricultural residues, wood residues and industrial residues (Twidell, 1998). Their costs and availability vary widely. Collection and transportation costs are often critical.

2.1.1 Agricultural residues

Sugar crops (cane and beet), starch crops (corn, wheat and barley), and sweet sorghum are agricultural crops presently grown commercially for both carbohydrate production and animal feeds. Large quantities of agricultural crop residues are produced annually worldwide and are vastly underutilized. One of the most common agricultural residues is the rice husk, which makes up 25% of rice by mass. Other plant residues such as sugar cane fiber (known as bagasse), corn stalks, wheat straws, coconut husks and shells, straw and miscanthus can be used (Demirbas, 2000).

2.1.2 Wood resources

Sawdust, bark, tree branches, tops of trunks, stumps and leaves represent a major resource for wood residues. When such wood residues have accumulated in abundance,

these residues have to be removed in order to reduce the risk of fires (Simpkins et al., 2006).

2.1.3 Energy crops

Energy crops, also called "bioenergy crops", are fast-growing crops that are grown especially for the specific purpose of producing energy (electricity or liquid fuels) from all or part of the plant. Energy crops include short rotation plantations such as eucalyptus, willows and poplars. Herbaceous crops, such as sorghum, sugarcane and artichokes, and vegetable oil bearing plants, such as soya beans, sunflowers. The optimal crop will vary with growing season and other environmental factors. Most fast-growing woody and annual crops are high in hemicellulose sugars such as xylose (Lauder, 2002).

2.1.4 Industrial residues

Industrial residues include mill wood wastes, urban wood wastes, agricultural processing wastes, mixed paper from municipal solid waste, cellulosic fiber fines from recycled paper mills, and bagasse from sugar manufacture. Each waste has unique characteristics, and often varies from one to another. Industrial residues with lower lignin contents and smaller particle sizes are easier to deal with than those with higher lignin contents and larger particle sizes. Waste paper that has been treated by a chemical pulping process is much more readily converted than in native wood or herbaceous residue (Jayasuriya and Soni, 2003).

2.2 Biomass composition and structure

Biomass and lignocellulosic materials compose mainly of carbohydrate polymers (holocellulose) and non-carbohydrate polymer (lignin), holocellulose includes cellulose

and hemicellulose. Cellulose composes 30-50% on a dry basis; it is a linear homopolymer of D-glucopyranose units bonded together through β -(1 \rightarrow 4) glucosidic bonds, this type of bonding and intra and intermolecular bonds give the crystalline and amorphous structures of cellulose, unlike starch which composes of D-glucopyranose linked together through α -(1 \rightarrow 4) glucosidic bonds, also it gives the cellulose the high tensile strength and make the fibers insoluble in most of the solvents. Degree of polymerization refers to the number of glucose units in the cellulose molecule. Hemicellulose composes of 20-40% of the biomass on dry basis, unlike cellulose, hemicellulose is branched polymer, the building units of hemicellulose are primarily six carbon sugars such as, D-glucose, D-mannose, D-galactose, and five carbon sugars such as D-xylose, L-arabinose, and the composition of hemicellulose varies between softwoods, hardwoods and grasses. It can be easily hydrolyzed by acids and solubilized in alkali due to its branched, amorphous nature. Lignin is a non-carbohydrate polymer and the largest non-carbohydrate fraction of lignocelluloses, it composes 15-25% of the total biomass on dry basis. The main role of lignin is to glue the cellulose and hemicellulose together. The lignin is made up of phenylpropane units in a three dimensional polymer, linked together mainly through C-C or C-O-C bonds, the methoxyl content in the phenylpropane units vary between softwoods, hardwoods and grasses (Roger, 2005).

Extractives referred to the chemicals that can be extracted from biomass using different solvents. The extractives are chemicals in the lumen of the cell, they are mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and many other minor organic compounds. Biomass contains a relatively small portion of inorganic compounds it varies from 0.1 to 12%; it is made up of Na, K, Mg,

Ca, S, N, P, Si, Al, and others. The remaining part after the combustion at $575 \pm 25 \text{ }^\circ\text{C}$ is called ash. Globally, forest biomass contains less inorganic matter than straw and cereals (Dokyoung et al., 2007; Roger, 2005).

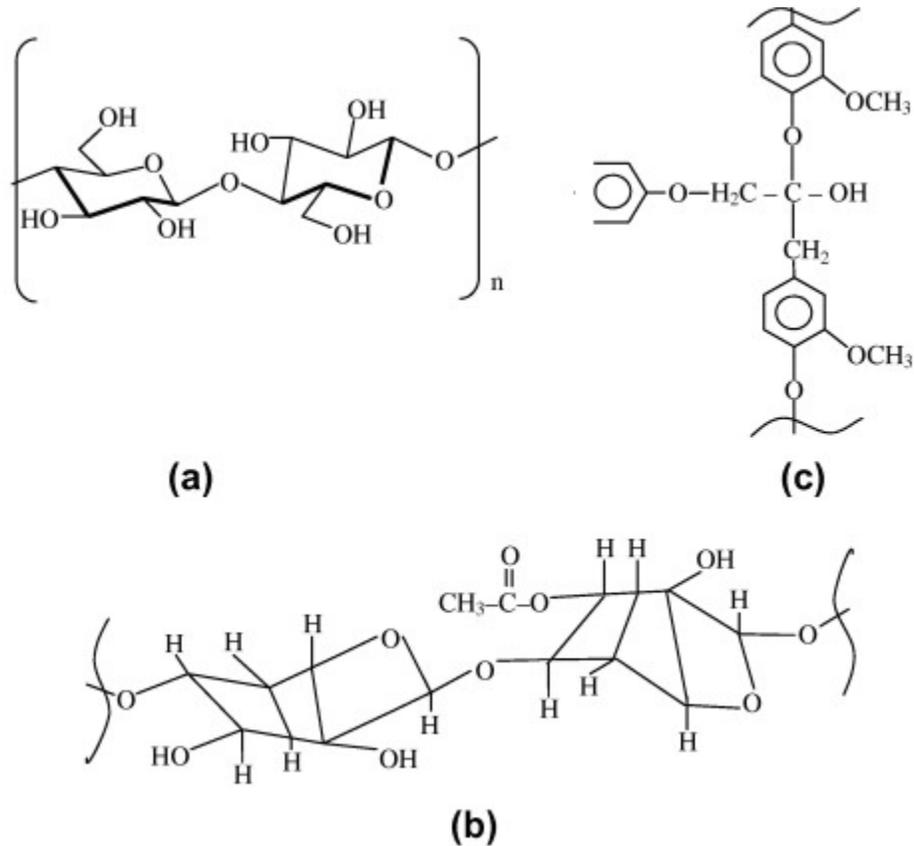


Figure 2.1 Chemical structure of (a) cellulose (b) hemicelluloses and (c) lignin (Bledzki and Gassan, 1999)

2.3 Biomass as source of energy

Biomass is a very promising renewable source of energy. Biomass includes all plants and plant-derived materials that are available on a renewable basis; it is a sustainable feedstock for the production of transportation fuels. There is growing

attention for the conversion of biomass into liquid energy in addition to direct combustion (Administration, 2009).

Biomass energy production contributed 4.3 quadrillion Btu of energy to the 75 quadrillion Btu of energy produced in the United States or about 5.7% of total energy production in 2010, the contribution of biomass converted to biofuels had tripled from 2005 to 2010. In 2012, biomass supplies are estimated to range from about 59 million dry tons at a farm gate price of \$40 per dry ton or less to 162 million dry tons at \$60 per dry ton. By 2030, quantities increase to 160 million dry tons at the lowest simulated price to 664 million dry tons at the highest simulated price (\$60 per dry ton). At prices above \$50 per dry ton, energy crops become the dominant resource after 2022 (Bob Boundy, 2011).

Giant miscanthus has received widespread attention as a perennial energy crop in the United States; it is native to Eastern Asia and now is grown in various temperate and tropical areas. It is one of the very promising energy crops because of its low water and ash content and high heating value, it can yield 10 to 15 tons/acre/year of dry matter compared to yields of 6-7 tons of dry matter for both corn and switchgrass (Iowa State University, 2010).

2.4 Biomass as source of chemicals

The abundant biomass resources of wood, grasses, and crop residues (lignocellulosic materials) are used to synthesize a large-volume of chemical feedstocks, which are converted in the chemical industry to a wide variety of more complex chemicals and materials. The large (polymer) molecules in lignocellulosic materials are converted to the desired chemical feedstocks by chemical means including treatment with

acids, alkaline chemicals, and various biological processes. The three basic polymers (lignin, cellulose, and hemicellulose) are reduced to sugars and various benzene-based aromatic chemicals, which can be synthesized to chemical feedstocks by rather direct and efficient chemical or fermentation methods (Goldstein, 1975).

The carbohydrate fraction can be processed to produce various products such as ethanol, lactic acid, furfural, or citric acid. Once the biomass chemical industry can supply the raw materials, low cost lactic acid will compete as a direct substitute for petrochemicals and take advantage of its own unique properties. Lactic acid forms lactide, and lactide can form polymers. These lactide polymers make transparent films and strong fibers and are biodegradable. Research and development for lactide polymers will tailor new products to meet requirements for specific end uses in direct competition to petrochemical polymers (Demirbas, 2000).

A solid residue is produced from the production of polymers from biomass. This solid residue is predominantly composed of lignin, it has high energy content so it is usually burned to produce process steam and electricity. There are other higher value uses for lignin, such as preparation of phenol formaldehyde resin that are useful as wood adhesives and injection molded plastics. It is also used for preparation of polyester, polyurethane and many other useful compounds (Broder and Barrier, 1988).

In the future biomass-derived chemicals could play an increasing role in the petrochemical industries. The economic decisions to use or not to use biomass would be based on an assessment of the overall process from feedstock to end product and probably involve consideration of various alternative synthesis routes in most cases. At present, however, too little information is available about the relative merits of biomass-

versus coal-derived chemicals to expect widespread, new industrial commitments to biomass chemicals in the near future (Werpy and Petersen, 2004).

2.5 Biomass conversion processes

The conversion technologies for converting the biomass into fuels and chemicals can be separated into three basic categories: thermochemical processes (combustion, pyrolysis, gasification and liquefaction), chemical and biochemical processes.

2.5.1 Pyrolysis

Pyrolysis is a thermochemical decomposition process in which the organic material is converted into a carbon-rich product and volatile matter by heating in the absence of oxygen (Demirbas and Arin, 2002). Relatively low temperatures are employed of 500-800 °C compared to 800-1000 °C in gasification. Three products are usually produced: gaseous (CO₂, H₂, CO, CH₄, C₂H₂, C₂H₄, C₂H₆, benzene, etc.), liquid products pyrolysis oil, also termed bio-oil and solid products (char).

The pyrolysis process can be adjusted to favor charcoal, liquid bio-oil, or gas production with a 95.5% fuel-to-feed efficiency. There are two types of pyrolysis: fast pyrolysis which is characterized by high heating rate and short residence time. Also, there is the slow pyrolysis which is performed at lower heating rates and lower temperature and relatively longer residence time, moreover, very fast pyrolysis is sometimes referred to as flash pyrolysis (Demirbas and Arin 2002).

Fast pyrolysis can produce high yields of bio-oil liquid product under optimized conditions: very high heating and heat transfer rates that require a finely ground biomass feed, carefully controlled temperature of around 500 °C and rapid

cooling of the pyrolysis vapours to give the bio-oil product. Bio-oil is a liquid mixture of oxygenated compounds containing various chemical functional groups, such as carbonyl, carboxyl and phenolic. Bio-oil is made up of the following constituents: 20-25% water, 25-30% water insoluble pyrolytic lignin, 5-12% organic acids, 5-10% non-polar hydrocarbons, 5-10% anhydrosugars and 10-25% other oxygenated compounds (Bridgwater and Peacocke, 2000).

Bio-oils derived from biomass have been increasingly attracting attention as alternative sources of fuels and chemicals, but some problems in the conversion process and use of the oil need to be overcome. These include poor thermal stability and corrosivity of the oil. The upgrading of this bio-oil by lowering the oxygen content and removing alkalis by means of hydrogenation and catalytic cracking of the oil is required for certain applications (Demirbas and Giillu, 1998).

2.5.2 Gasification

Gasification is a form of pyrolysis, which is performed at high temperatures (800-1000 °C) in order to optimize gas production. The mainly used reaction media are air and oxygen/steam. The process can work either at atmospheric pressure, or be pressurized. The resulting gas, known as producer gas or syngas, is a mixture of carbon monoxide, hydrogen and methane, along with carbon dioxide and nitrogen. The gas is more versatile than the original solid biomass (usually wood or charcoal). It can be burnt to produce heat and steam, or used in gas turbines to produce electricity. Biomass is normally converted to gasification products through a gasifier system (Craig and Mann, 1996). Numerous types of gasifiers have been developed and tested and many industrial applications can

use the technology. The most common types are updraft and downdraft gasifiers, counter and co-current fixed bed, bubbling and fluidized beds (Wilén and Kurkela, 1997).

2.5.3 Liquefaction

Liquefaction is the conversion of the biomass into liquid products. The first attempt to liquefy wood began in 1925 (Fierz-David, 1925). Numerous studies have been reported on the liquefaction of biomass. The primary objective has always been conversion of lignocellulosic materials into fuel and chemicals. Liquefaction of biomass and wastes can be accomplished by thermochemical (direct or indirect) or chemical methods (Appell et al., 1971).

2.5.3.1 Direct liquefaction

Direct liquefaction is the reaction of biomass components with small molecules such as H₂ and CO or short-term pyrolytic treatment, sometimes in the presence metal salts as a catalyst. Indirect liquefaction involves successive production of an intermediate, such as synthesis gas or ethylene, and its chemical conversion to liquid fuel. The typical direct liquefaction process is conducted under high pressure, at high temperature (300-500 °C) and sometimes in the presence of a catalyst (metal salts) and/or reducing gases, e.g. hydrogen (Maldas and Shiraishi, 1997). An example for direct liquefaction process involves reacting carbon monoxide with wood particles in the presence of a sodium carbonate solution as a catalyst at up to a temperature of 371 °C and up to 4000 psi to produce oil or water slurries. Carbon monoxide reacts with sodium carbonate in the presence of water to form sodium formate which, in turn, reacts with cellulose in the wood to form oil and regenerate sodium carbonate (Friedman et al., 1977).

2.5.3.2 Chemical liquefaction

Shiraishi (1983) discovered that chemically-modified wood can be dissolved in several neutral organic solvents or aqueous solutions. This has opened the door to chemical liquefaction. Since that time, liquefaction of lignocellulosic and other biomass in the presence of some organic solvents represents one of the most promising approaches for the utilization of lignocellulosic biomass (Maldas and Kokta, 1993; Worthy, 1990). The liquefied products could be used as a source of chemicals rather than utilizing the fossil fuels. Through liquefaction, wood components, cellulose, hemicelluloses and lignin are converted to low molecular weight compounds with high reactivity. The liquefied lignocellulosics have many potential applications such as preparation of polyurethane foams, films, carbon fiber, preparation of novolak-type phenolic resins, preparation of adhesives for plywood. It is also used for preparation of epoxy resin (Kobayashi et al., 2000).

2.5.3.3 Hydrothermal liquefaction

Research on hydrothermal liquefaction began in the late 1970's and early 1980's especially when the oil crisis had started. Hydrothermal liquefaction is one of the thermochemical methods for the conversion of biomass; it is generally performed at 280-370 °C and between 10-25 MPa (Behrendt F, 2008). At these conditions water has a range of exotic properties. Liquid water at standard conditions ($T = 25\text{ °C}$, $P = 0.1\text{ MPa}$) is poorly miscible with hydrocarbons. However, water in the critical range ($T = 374\text{ °C}$, $P = 22\text{ MPa}$) is a very good solvent for non-polar molecules, due to its low dielectric constant and poor hydrogen bonding. Viscosity and dielectric both decrease at this range. For these reasons, water is an important reactant and catalyst simultaneously, and thus the

biomass can be directly converted without an energy consuming drying step, as in the case of pyrolysis (Bridgwater et al., 1999).

Water in the subcritical state was used to successfully hydrolyze triglycerides in soybean, linseed and coconut oils in a temperature range of 260-280 °C with conversion of greater than 97% after 15-20 min (Holliday et al., 1997). Total cellulose conversion was achieved within 2 min at 280 °C. Rather than the release of glucose, cellulose hydrolysis rate in water increased tenfold between 240 and 310 °C at 25 MPa. The decomposition of cellulose becomes a dominant process in the temperature range between 250-270 °C (Toor et al., 2011). On the other hand, lignin is much more resistant to degradation (Bobleter, 1994). The effects of the homogeneous catalysts and heterogeneous catalysts on glucose reactions in hot compressed water (200 °C) have been investigated. Homogeneous acid catalysts enabled dehydration, and the isomerization of glucose to fructose was promoted by alkali (Watanabe et al., 2005).

2.5.3.4 Alcohols-water liquefaction

Conventional hydrothermal liquefaction processes need to be run under high pressure and temperature; the high critical point of water makes the process less economically effective since the energy inputs to perform the process is relatively high. Wood and other lignocellulosic materials can be easily liquefied at a low temperatures and atmospheric pressures in the presence of phenol and acids such as sulfuric, phosphoric and oxalic acids. With this application of phenol and acids more than 30 compounds were obtained as the main reaction products and the dominant products were guaiacylglycerol- α -phenyl- β -guaiacyl ethers, followed by guaiacol, triphenylethanes, diphenylmethanes, benzocyclobutanes and phenylcoumarans (Lin et al., 2001). However,

disadvantages are that strong acids which can cause corrosion for the equipment used in the process. Hydrochloric and phosphoric acids are preferred for biomass liquefaction with phenols at low temperatures. However, the price of phenol is relatively high when compared to other solvents and the recycling of the phenol is a difficult process. Later on, many studies were performed using other solvents for more economically and environmentally liquefaction.

The liquefaction process was performed using phenol/lower alcohol mixtures and methanesulfonic acid as a catalyst. When 60% of phenol was replaced with alcohols the amount of residue was slightly increased and the minimum residue was obtained at 190 °C for a residence time less than 90 min. Results showed that short alkyl chain alcohols were effective for the liquefaction (Hassan and Mun, 2002). Lignocellulosic materials were liquefied using ethylene carbonate or propylene carbonate in the presence of acid catalyst at elevated temperatures (120-150 °C). A very rapid and complete liquefaction of cellulose and white birch occurred in the ethylene carbonate. The liquefaction process was not accomplished because of the formation of insoluble lignin derivatives when applied to softwood although the rate of ethylene carbonate liquefaction of cellulose was almost 10 times faster than that of polyhydric alcohols liquefaction (Yamada and Ono, 1999).

The liquefaction of jack pine (*Pinus banksiana*) was performed in sub and supercritical ethanol with and without iron-based catalysts at a temperature of 200-350 °C and initial pressure of hydrogen ranging from 2-10 MPa. The yield of oil increased from 17-44% to 63% when a catalyst was added at 350 °C, 5 MPa of H₂ and for 40 min of time. Phenolic compounds were dominant in the oils, irrespective of whether or what

catalyst was used. The liquefaction of Japanese beech (*Fagus crenata*) was studied with various subcritical and supercritical straight-chain alcohols. Below 270 °C and for 30 min, beech wood was liquefied in all alcohols with 50-65% insoluble residue, however, below 350 °C; more than 90% of the wood was decomposed and liquefied in all alcohols. Furthermore, the study showed that alcohols with longer alkyl chains liquefy lignocellulosic materials at shorter residence times (Yamazaki et al., 2006).

The effect of various solvents (water, acetone, and ethanol) was studied for the liquefaction of biomass in the temperature range 250-450 °C and initial pressure of 1 MPa for 20 min. Acetone had the highest conversion rate and the highest oil yield reached 26.5% in ethanol at 200 °C. Supercritical alcohols can be used as a solvent and also as a hydrogen donor and reactant in the form of hydroxyalkylation and deoxygenation reactions. GC-MS showed the presence of phenolic compounds mainly derived from the basic coniferyl alcohol units of lignin (Liu and Zhang, 2008).

Swine manure was liquefied to bio-oil using ethanol as solvent without catalyst under a temperature range of 240-360 °C. The main important factor was the reaction temperature and a heating value of 33.98 MJ/Kg was obtained at reaction temperature of 300 °C. FTIR analysis of the bio-oil produced showed that a low content of carbonyl and aliphatic groups and a high aromaticity in the bio-oil resulted. The efficiency of supercritical methanol to convert woody biomass into bio-oil at modest temperatures (> 238 °C) and pressures (> 8.1 MPa) was studied. Results showed that the liquefaction process of woody biomass can be achieved of 90 wt% conversion. The bio-oil composed of partially methylated lignin-derived monomers and sugar derivatives could also be upgraded into a drop-in-fuel. (Baskar et al., 2012; Xiu et al., 2010)

Bagasse was liquefied in the presence of supercritical ethanol with or without various proportions of water as a proton donor under hydrogen pressure, and for catalyst types (FeS, Fe₂S₃/activated carbon, and FeSO₄). A 59.6% yield of bio-oil and 89.8% biomass conversion were obtained with 100% (v/v) ethanol without catalyst. The catalyzed reaction with FeSO₄ yielded an oil yield of 73.8% and biomass conversion of 99.9%. The bio-oil obtained had a heating value of 26.8 MJ/Kg (Chumpoo and Prasassarakich, 2010). The effect of wood species on the liquefaction in polyethylene glycol (PEG) or glycerol containing PEG was studied. A yield of 10-30% of residual materials was obtained using the PEG system. The addition of 10% of glycerol to the PEG system resulted in small amount of residual materials (~3%) and a stable hydroxyl number regardless of the wood species (Kurimoto et al., 1999).

The effect of three alcoholic solvents; monohydric n-octanol, dihydric ethylene glycol, and trihydric glycerol on biomass liquefaction was studied by thermogravimetric analysis. The results indicated that some molecular or functional groups of biomass are likely to be alcoholized to form new molecules and to facilitate the liquefaction of biomass. Results also showed that the highest liquefaction yield of 83.54 wt% was obtained with n-octanol. However, the liquefaction yield of biomass with polyhydric alcoholic solvents were less than 60 wt% suggesting that biomass cracks more easily when mixed with monohydric n-octanol than with polyhydric alcohols. The contents of net light oil from biomass liquefaction with polyhydric alcohol solvents are almost negligible when compared to those of the heavy oil and residue. This result indicates that condensation and polymerization reactions take place among some parts of depolymerized and degraded compounds from biomass liquefaction with polyhydric

alcoholic solvents. The main three polymers of biomass can be alcoholized with acidic catalyst, the intermediates include glucose and xylose from cellulose and hemicellulose degradation and also from the lignin, these intermediates can react further with alcoholic solvents (Xianwu Zou, 2009).

2.6 Bio-oil upgrading

Crude bio-oil produced by pyrolysis is dark brown complex mixture, it is viscose and composes of many compounds such as phenolic compounds, acids, aldehydes, ketones, esters, sugars, guaiacols, syringols, furans (Guo Yan, 2001). The presence of these compounds causes the chemical instability and its high acidity. Bio-oil contains substantial amounts of carboxylic acids, such as acetic acid and formic acids. The bio-oil of pine woods had a pH of 2.6, however, the pH of hardwood bio-oil was 2.8 (Sipila et al., 1998). Thus, the upgrading of bio-oil is an important process to increase the chemical and thermal stability of bio-oil and to decrease its corrosiveness and its viscosity through decreasing the oxygen content and the conversion to more stable compounds. Bio-oil contains more than 300 different compounds resulting from the decomposition and depolymerization of polymer present in lignocellulosic materials and the specific composition of the bio-oil depends on the feed and the conditions of the process (Zhang et al., 2007).

The main difference between the bio-oil and hydrocarbon fuels is the presence of oxygen which leads to decrease the energy density by 50% of conventional fossil fuels and immiscibility with the hydrocarbons produced from fossil sources (Zhang et al., 2007). Oxygen could be removed as H₂O and CO₂ by a hydrodeoxygenation process under hydrogen pressure catalyzed by Co-Mo, Ni-Mo and their oxides or loaded on

Al₂O₃ which increases the energy density of the product (Pindoria et al., 1997). In an autoclave and in the presence of tetraline as a hydrogen donor solvent under 360 °C and 2 MPa of hydrogen pressure, the oil phase of 70% crude bio-oil was hydrotreated and catalyzed by sulphided Co-Mo-P/Al₂O₃ reducing the oxygen content from 41.8% to 3% after the upgrading (Zhang et al., 2005). Adjaye and Bakhshi (1995) found that HZSM-5 was the most effective catalyst compared to zeolite H-Y, H-mordenite, silicalite and silica-alumina under a temperature range of 290-410 °C.

Guo Xiaoya (2003) reviewed various catalysts used in bio-oil upgrading in detail and stated that although catalytic cracking is a predominant technique producing a high conversion and little coking tendency has get to be achieved. Although catalytic cracking is regarded as a cheaper route by converting oxygenated feedstocks to lighter fractions, the results have not been promising due to high coking (8–25 wt%) and poor quality of the fuels obtained (Zhang et al., 2007). Crude algal bio-oil produced from hydrothermal liquefaction of a microalgae was also upgraded in supercritical water under high pressure of hydrogen catalyzed by Pt/C catalyst. The upgraded bio-oil had a higher heating value ~42 MJ/Kg and lower acid number; also it was lower in oxygen and nitrogen and free of sulfur. The Pt/C led to high abundance of hydrocarbons in the upgraded bio-oil (Duan P, 2011).

2.6.1 Bio-oil upgrading through esterification process

The upgrading of bio-oil produced from fast pyrolysis of *Pinus sylvestris* was conducted over supported noble metal catalysts in supercritical monoalcohols under a hydrogen atmosphere. Many reaction mechanisms such as esterification, cracking (both alcoholysis and hydrolysis), hydrogenation, along with acetalization, isomerization, and

other reactions were combined during the upgrading process. Good results were obtained when ethanol over Pt/SO₄⁻/ZrO₂/SBA-15 were used and it showed that the upgrading process can be applied to the whole bio-oil without fractionation (Zhang et al., 2012). The bio-oil obtained from fast pyrolysis of rice husk was upgraded in supercritical ethanol in the presence of aluminum silicate as a catalyst. It can be demonstrated that bio-oil was effectively upgraded and esterified and the aluminum silicate which has an acidic effect facilitates the esterification and the conversion of acids in the bio-oil. Phenols and aldehydes were successfully removed during the upgrading process. The density and viscosity of the upgraded bio-oil were also decreased and the pH and heating value were increased (Peng et al., 2008).

The bio-oil from mallee wood was upgraded in methanol catalyzed by commercial solid acid catalyst (Amberlyst-70) over a temperature range of 70 to 170 °C. Results showed that light organic acids in the bio-oil were converted into stable esters. Aldehydes as well were converted through acetalization. The acetalization was strongly affected by the temperature of the reaction as high temperature caused further decomposition of acetals (Gunawan et al., 2011). Upgrading reactions of the high-boiling fraction of bio-oil using supercritical methanol over a series of supported mono and bi-metallic catalysts were also studied (Li et al., 2011). Esterification and cracking were the two dominant processes. A high yield of 72.4 wt% of refined bio-oil was obtained when PtNi/MgO catalyst was used. This acidic catalyst produced lower product yields but it tended to inhibit coking reactions.

The effect of esterification conditions on reaction conversion of palm shell bio-oil using alcohols and acid catalysts was studied (Weerachanchai et al., 2012). When

Amberlyst 15 was used as an acidic catalyst, the organic acids in the bio-oil were converted into esters and the aldehyde amount was reduced. Moderate heating value (23-25 MJ/Kg) was obtained and other properties such as density, viscosity and carbon residue content were improved. Although H_2SO_4 can be used to give higher reaction conversion to esters, higher temperatures, longer reaction times, higher amounts of catalyst and shorter hydrocarbon alcohol chains are required.

The objective of this study was to optimize the low-temperature hydrothermal liquefaction of giant miscanthus with alcohol as co-solvent and to upgrade the bio-oil produced. More specifically, our target was the optimization of parameters and conditions which affect the liquefaction process, the reduction of reaction time and energy inputs applied in the process, and characterization of the produced bio-oil chemically and physically. Secondly, the upgrading the bio-oil using different catalysts, to produced more chemically and thermally stable bio-oil. The other main objective was to develop a new approach of liquefaction and upgrading process in one step to liquefy the biomass with high quality bio-oil yield in one step at relatively lower reaction time and temperature.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Giant miscanthus biomass was obtained from the south farm in Mississippi. The biomass was first air dried then ground in a Wiley mill and sieved. The miscanthus powder of 40-80 mesh size was fractionated and used in this study.

3.2 Chemicals

All chemicals used in this study were purchased from commercial resources and used without further purification. Ethanol, dichloromethane, zinc chloride, sodium carbonate, trifluoroacetic acid, formic acid, aluminum silicates, zeolite ZSM-5 and filter paper were purchased from Fisher Scientific International Inc. Sugar standards such as D(+)-glucose, D(+)-xylose, D(+)-galactose, L(+)-arabinose, D(+)-mannose and dextran with different molecular weights (1000-80000 Da) used for chemical composition analysis were purchased from Sigma-Aldrich Corporation. Zeolite Y CBV400 was purchased from Zeolyst International.

3.3 Chemical analysis of the biomass

Giant miscanthus biomass was extracted with a mixture of ethanol and benzene (1:1) using the soxhlet for 6 hours to remove water insoluble compounds. 10 g of air dried giant miscanthus biomass were placed in a thimble in a 500 ml flask containing 300

ml of ethanol/benzene mixture. After the extraction, the sample was dried at room temperature overnight and stored for moisture conditioning. Klason lignin was determined using two step acid hydrolysis. Extractive-free biomass of 3 g was first hydrolyzed in 3 mL of 72% of sulfuric acid H_2SO_4 for one hour. Concentrated acid was then diluted to 4% H_2SO_4 by adding 84 mL of deionized water. The sample was then put in a pressure tube and was kept in the autoclave for one hour at 121 °C to completely convert all oligomeric sugars into monomers. After cooling, this mixture was filtrated using a medium size crucible of 30 mL, and then the crucible was put into an oven at 105 ±3 °C overnight. Hydrolyzed sugar solution was neutralized using calcium carbonate to reach a pH = 6. High Performance Liquid Chromatography (HPLC) Agilent 1200 was used to analyze the monomer sugars. Acid soluble lignin was determined using UV-Vis spectrophotometer (Cary 100 Bio). The range of wavelength was from 200 to 400 nm and the UV absorbance was at 275-278 nm. For ash determination, approximately 7 g of biomass was weighed and put into the crucible which was placed into a the furnace at 575 ±25 °C for 6 hours, it was kept covered in the beginning to avoid the loss of the sample during the initial burning process, but the cover was removed after caring for the loss was over. The crucible was then removed and kept in a dessicator to cool and the weight of ash was then determined after cooling. Giant miscanthus biomass was extracted, hydrolyzed, analyzed by Klason lignin test and ash content test according to methods applied by Sluiter et al (Sluiter et al., 2005a; Sluiter et al., 2008; Sluiter et al., 2005b).

3.4 Liquefaction of biomass

Liquefaction of giant miscanthus biomass (40-60 mesh) was performed in a 450 mL high pressure Parr reactor (5500 series) equipped with a stirrer as shown in Figure

3.1. The reactor was charged with the biomass and water or ethanol-water co-solvent. After charging the reactor with the biomass and liquefying agent, the reactor was sealed and the air inside the reactor was purged with high-purity nitrogen for 3-5 times. The reactor was subsequently pressurized with nitrogen to prevent the reactive material from boiling in the course of the heating process. The reactor was ramped up to the desired temperature (200-280 °C) at a heating rate of 15 °C/min. The temperature was kept constant during the reaction (5-60 min). Following the liquefaction, the reactor was rapidly cooled in ice-water to room temperature. After cooling, the liquid products and solid residue in the reactor were completely washed with excess ethanol, filtered under reduced pressure through a pre-weighed Whatman grade 4 filter paper and dried in the oven at 105 °C for 6 hours before weighing. The excess of ethanol in the filtrate was removed by rotary evaporator under reduced pressure at 50 °C. The water in the remaining portion was removed through the extraction process with dichloromethane with a separating funnel to separate the bio-oil and solvent portion from the aqueous portion. Dichloromethane was then removed using a rotary evaporator under reduced pressure at 40 °C. Figure 3.2 shows a diagram of the procedure of separation of liquefied and solid residue products. The yield of solid residue was calculated based on the oven dry weight of biomass and expressed in % (w/w) according to equations (3.1) to (3.3)

$$\text{Solid residue (\%)} = \frac{(\text{Dry weight of solid residue})}{(\text{Dry weight of biomass})} \times 100 \quad (3.1)$$

$$\text{Bio – oil yield (\%)} = \frac{(\text{Weight of bio–oil})}{(\text{Dry weight of biomass})} \times 100 \quad (3.2)$$

$$\text{Biomass conversion (\%)} = 100 \% - \text{solid residue \%} \quad (3.3)$$

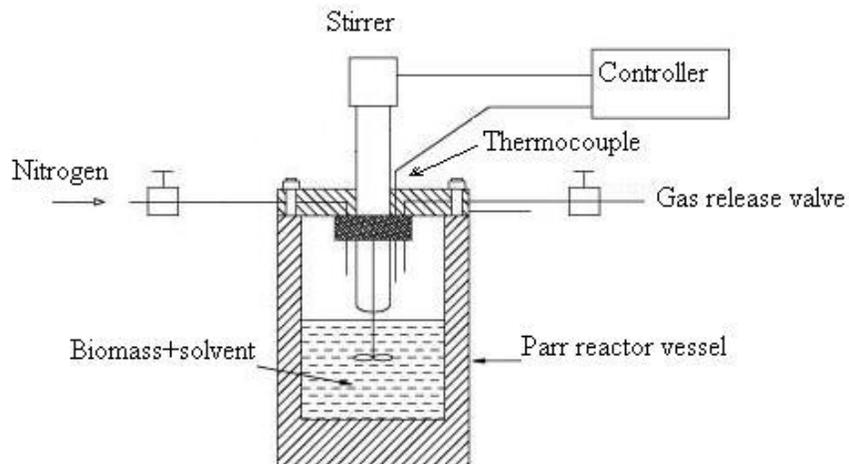


Figure 3.1 Schematic representation of the hydrothermal reaction system. Modified from (Yu et al., 2012)

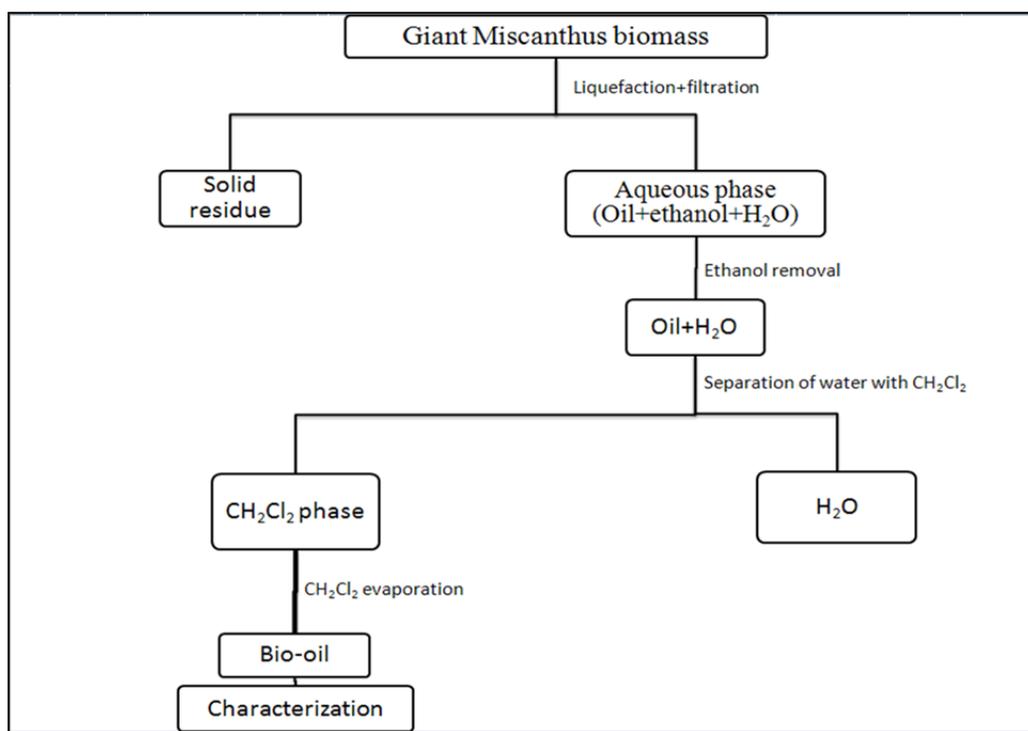


Figure 3.2 Procedure for separation of hydrothermal liquefaction products.

3.5 Bio-oil conventional upgrading

Crude bio-oil and ethanol mixture produced from the liquefaction at the optimum conditions was upgraded and esterified using supercritical ethanol at 280 °C. The yield of bio-oil in the ethanol was calculated based on the data of bio-oil yield obtained at the optimum conditions. For the upgrading experiment, water was removed from the bio-oil by fractionation step using dichloromethane solvent followed by evaporation of CH₂Cl₂ using a rotary evaporator at 40 °C under reduced pressure. An equivalent amount of ethanol was added to the crude bio-oil and the resultant mixture of bio-oil plus excess of ethanol was used for upgrading and esterification process. Two different types of catalysts were chosen for the study; zeolite Y CBV400 and zeolite ZSM-5. The weight of applied catalyst was 20% (w/w) based on the amount of bio-oil. Reaction conditions were 280 °C for the temperature applied for 1 hour, with initial hydrogen pressure of 1 MPa. At the end of the experiment, the vessel content was cooled and filtered using Whatman grade 4 filter paper to separate the solid portion representing the catalyst. The upgraded bio-oil (filtrate) was characterized using GC-MS and FTIR. Heating value was measured as well.

3.6 One step liquefaction and upgrading of biomass

Liquefaction and upgrading of giant miscanthus was performed in one step by adding solid acid catalysts during the liquefaction process. Four different catalysts and catalyst combinations were chosen for the experiments; aluminum silicate, zeolite Y CBV400, aluminum silicate/zinc chloride, and zeolite/zinc chloride. The amount of added catalyst in each experiment was 25% (w/w) based on the original dry weight of biomass. For the combined catalysts, the total ratio of catalyst to the biomass was 27%

(25% zeolite of aluminum silicate and 2% of zinc chloride). All experiments were conducted in the Parr[®] 5500 series reactor for 1 hour at temperature of 280 °C. The initial hydrogen pressure was 1 MPa and a co-solvent of 80% ethanol and 20% water was used for all experiments. At the end of each experiment, the vessel was cooled, and the content was filtered using Whatman grade 4 filter paper. The solid portion containing the catalyst and the unreacted biomass was dried at 105 °C for 6 h and the residue content was calculated by subtracting the initial weight of catalyst from total weight of the solid residue. Water was removed from the liquid fraction composed of oil, water and ethanol using methylene chloride solvent with subsequent evaporation of the solvent with a rotary evaporator at 40 °C under reduced pressure. The liquefied part was characterized by GC-MS. Heating value was measured as well.

3.7 Gas chromatography mass spectrometry (GC-MS) analysis

The quantitative GC-MS analyses of the crude and upgraded bio-oils were performed with a Hewlett- Packard HP 5890-Series II gas chromatograph (GC) equipped with a Hewlett-Packard HP 5971 series mass detector (MS). For crude bio-oil, the liquefaction solvents (water and ethanol) were firstly removed according to the above prescribed separation method in Figure 3.2. A representative sample (0.2 g) of each bio-oil was weighed to the nearest 0.1 mg and diluted to 10.00 mL with methanol. For the upgraded bio-oil, the sample weight was taken directly (0.2 g) and diluted to 10 mL with methanol. One mL of the diluted solution was transferred to an auto-sampler vial and 1.00 µl was injected onto a J&W Scientific Durabond HP-5MS, 30 m fused silica capillary column, 0.25 mm i.d. and 0.25 µm film thickness, using helium (99.99% purity) as the carrier gas with a constant flow rate mode at 1 mL/min. The initial oven

temperature of the GC was set at 40 °C for 4 min and the temperature then programmed at a rate of 5 °C/min to 270 °C. The final temperature was kept for 15 min and the total time of each run was 65 min. The injector and detector temperatures were 270 and 250 °C, respectively. The m/z (ratio of mass to charge) values, which represent the fragment ions of the compounds were recorded for each compound.

3.8 Elemental analysis and heating value

The heating value of crude bio-oil samples was calculated by using an Exeter Analytical Incorporation (EAI CE-440) elemental analyzer. The amount of (C, H and N) was determined experimentally and the amount of oxygen was determined by difference. The higher heating value for the bio-oil was calculated from Dulong's equation. Dulong's formula is a mathematical model used to calculate heating value based on elemental composition of the sample, the mass % of nitrogen is not included in the formula. The equation (3.4) of Dulong's formula was recommended for use by (Demirbas, 2006).

$$\text{Heating value (MJ/kg)} = \frac{33.5 \cdot \text{wt \%C}}{100} + \frac{142.3 \cdot \text{wt \%H}}{100} + \frac{15.4 \cdot \text{wt \%O}}{100} \quad (3.4)$$

3.9 Fourier transform infrared spectroscopy (FTIR)

The crude and upgraded bio-oils' functional group compositional analyses were investigated by FTIR Spectrophotometer (Varian 3100 FTIR). All measurements were performed with the KBr disc technique.

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Chemical composition of giant miscanthus biomass

There are slight differences in the chemical composition between different biomass resources. Generally, wood contains more lignin than grasses; however, grasses contain more holocellulose than wood. Moreover, the composition of hemicellulose and lignin vary between wood and grasses. The high portion of holocellulose in grasses makes it more easily converted than other biomass. Chemical analyses for giant miscanthus are shown in Table 4.1.

Table 4.1 Chemical composition and elemental analysis of giant miscanthus biomass

| Analysis | Wt. % |
|------------------------|-------|
| Chemical composition | |
| Glucose | 42.8 |
| Xylose | 20.7 |
| Galactose | 1.3 |
| Arabinose | 2.1 |
| Mannose | 2.1 |
| Lignin | 24.8 |
| Ash | 2.3 |
| Elemental analysis (%) | |
| Carbon | 46.0 |
| Hydrogen | 6.24 |
| Nitrogen | 0.18 |
| Oxygen (by difference) | 47.54 |
| Heating value (MJ/Kg) | 16.97 |

It is clear from Table 4.1 that giant miscanthus has a relatively high proportion of holocellulose (69%). Ash content was (2.3%) and (24.8%) of lignin. Xylose was the major hemicelluloses in giant miscanthus at 20.7%. The elemental composition of giant miscanthus was also performed and the heating value was calculated according to Dulong's formula. Analysis showed that giant miscanthus had a 16.97 MJ/Kg heating value which is very similar to woody products.

4.2 Optimization of liquefaction process

4.2.1 Effect of temperature

Temperature is the most important factor in the liquefaction process besides the ethanol to water ratio. It directly affects the reaction mechanisms during the liquefaction process.

The effect of temperature and ethanol to water ratio was not studied separately; however, different combinations of temperatures and ethanol to water ratios were applied to study the effect of both factors together and the interaction between them. High temperature at all ethanol to water ratios is necessary to break down high molecular weight polymers of the biomass. Unlike cellulose and hemicellulose, lignin requires a relatively higher temperature to be depolymerized. Figure 4.1 depicts the effect of temperature on solid residue yield at various ethanol to water ratios. It is clear from the figure that increasing the temperature from 220 to 280 °C was very effective in decreasing the amount of residue and accordingly in increasing the liquefaction yield. At 220 °C, more than 45% of biomass remained as residue at all ethanol to water ratios. At

280 °C less than 10% of residue remained at 50:50 ethanol to water ratio. Reaction temperatures below 280 °C will lead to incomplete liquefaction of the biomass.

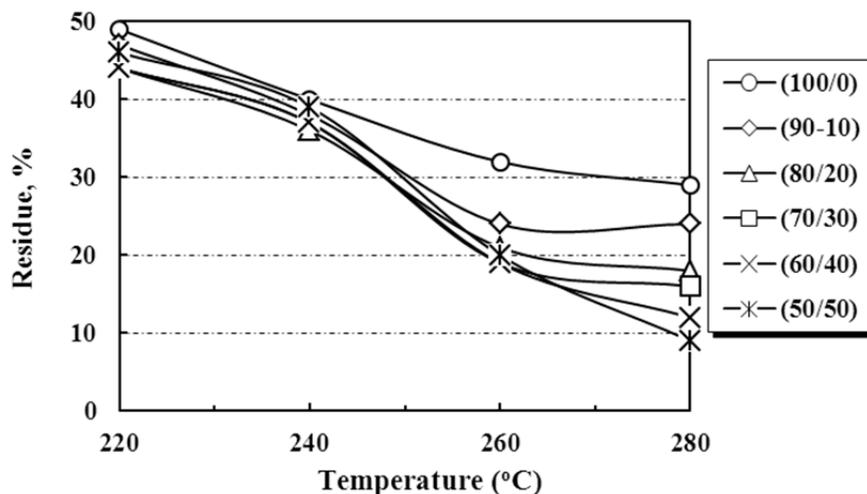


Figure 4.1 Effect of various temperatures at different ethanol to water ratios on the solid residue yield (Initial N₂ pressure = 4 MPa, reaction time = 30 min and biomass to solvent ratio = 1:8 w/w).

Figure 4.2 shows that the effect of temperature on the bio-oil yield had the same trend as in the case of solid residue, the bio-oil increased steadily when the temperature increased from 220 to 280 °C. More than 45% bio-oil yield obtained at 280 °C and at higher ethanol to water ratio. Accordingly, higher temperatures are required in order to obtain high bio-oil yield. Temperatures below 280 °C were not enough to obtain a high oil yield with low solid residue. Thermodynamically, the pressure increased during the reaction when the temperature went up and due to safety issues, the maximum pressure that could be allowed was 3000 psi.

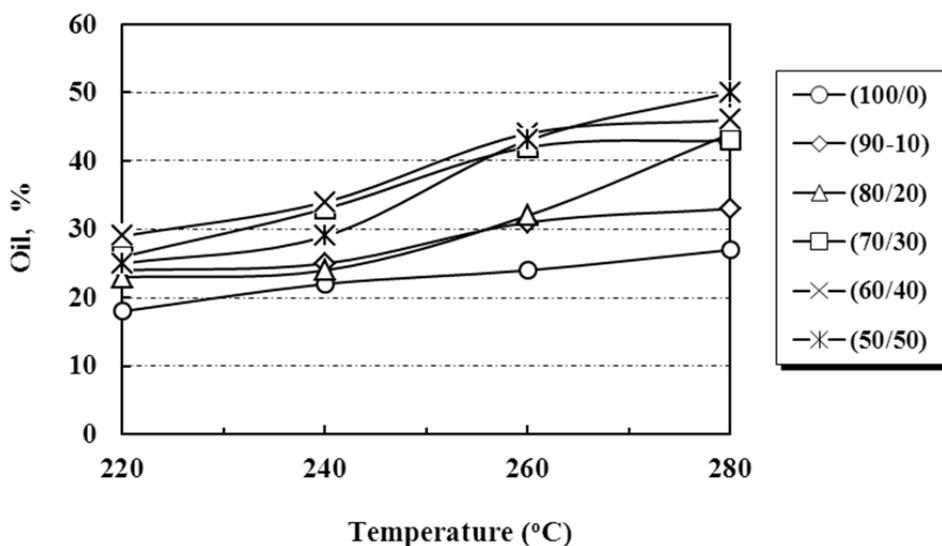


Figure 4.2 Effect of various temperatures at different ethanol to water ratios on the crude bio-oil yield (Initial N₂ pressure = 4 MPa, reaction time = 30 min and biomass to solvent ratio = 1:8 w/w).

4.2.2 Effect of alcohol to water ratio

Ethanol to water ratio and temperature are considered to be the primary factors during the process of liquefaction. The critical point of water exists at 374 °C and 220 bar while the critical point of ethanol is at 241 °C and 63 bar. A mixture of ethanol and water has a proportional critical point depending on the amount of ethanol as shown in Table 4.2. Therefore, the presence of ethanol in the reaction aids in performing the liquefaction process at much lower temperature and pressure conditions than when water alone was used. Therefore, lower energy is required for the reaction.

Table 4.2 The critical parameters of water-ethanol mixtures.(Abdurashidova et al., 2007)

| % of ethanol | T critical, °C | ρ critical, Kg/m ³ | P critical, MPa |
|--------------|----------------|------------------------------------|-----------------|
| 0 | 374.10 | 322.0 | 22.06 |
| 20 | 325.15 | 308.4 | 15.54 |
| 50 | 280.15 | 293.9 | 10.6 |
| 80 | 255.15 | 282.5 | 7.52 |
| 100 | 240.90 | 276.0 | 6.13 |

Figure 4.3 shows the effect of ethanol to water ratio on the amount of residue remained after liquefaction. It is evident from the figure that the amount of ethanol slightly affects the yield of residue at relatively lower temperatures of 220 and 240 °C. At higher liquefaction temperatures 260 °C and 280 °C an increasing in the amount of ethanol from 0 to 50% showed a positive effect on the liquefaction process and a pronounced decrease in the yield of residue was obtained. The amount of solid residue reached a minimum 9% at the highest studied ethanol to water ratio 50:50 and a 280 °C temperature. Also, at the optimum ethanol to water ratio 50:50, the amount of residue decreased from 29% at 220 °C to 9% at 280 °C. Accordingly, increasing the amount of ethanol to 50% and temperature to 280 °C has the best effect on the liquefaction process.

Figure 4.4 shows the effect of ethanol to water ratio on the oil yield of the liquefaction process. At low liquefaction temperatures 220 °C and 240 °C, the effect of increasing ethanol in the liquefaction system from 0 to 50% was minimal. The yield of bio-oil increased from 18 to 25% at 220 °C and from 22 to 29% at 240 °C. On the other hand, increasing the amount of ethanol from 0 to 50% at higher temperatures showed a pronounced improvement in the oil yield. The yield of the oil was increased from 24 to 43% at 260 °C and from 27 to 50% at 280 °C.

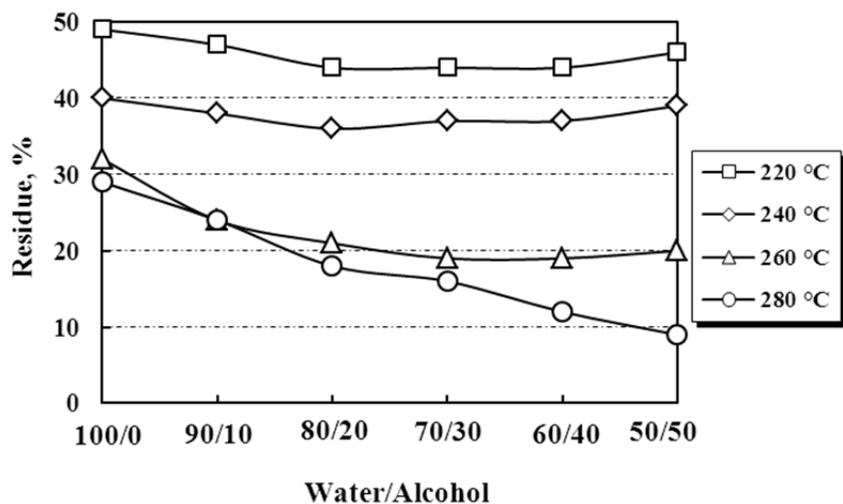


Figure 4.3 The effect of ethanol to water ratio at various temperatures on the solid residue yield (Initial N₂ pressure = 4 MPa, reaction time = 30 min and biomass to solvent ratio = 1:8 w/w).

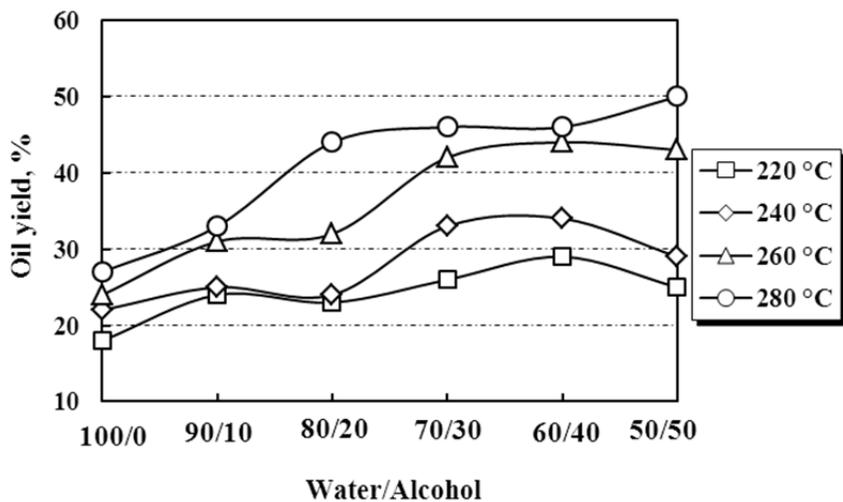


Figure 4.4 The effect of ethanol to water ratio at various temperatures on crude bio-oil yield (Initial N₂ pressure = 4 MPa, reaction time = 30 min and biomass to solvent ratio = 1:8 w/w).

4.2.3 Effect of time

The effect of reaction time on the yields of residue, oil and on the heating value of oil fraction at the optimum temperature 280 °C and ethanol to water ratio 50:50 was studied and the results are shown in Figure 4.5.

It is clear from the figure that the liquefaction of giant miscanthus at optimum temperature and ethanol to water ratio was efficiently performed at low reaction times 5-30 min. A bio-oil with 47% yield and 25 MJ/Kg heating value was obtained after 5 min; the residue content was almost 19%. Increasing the liquefaction time to 15 min increased the yield to 51% and decreased the residue to less than 8% with only a slight change in the heating value. Increasing the time from 20 to 30 min had a very small effect on both oil and residue yield but the heating value was increased slightly to 26 MJ/Kg. Based on the values of oil yield, amount of residue and heating value, applying 15 min reaction time is ideal for liquefaction of giant miscanthus.

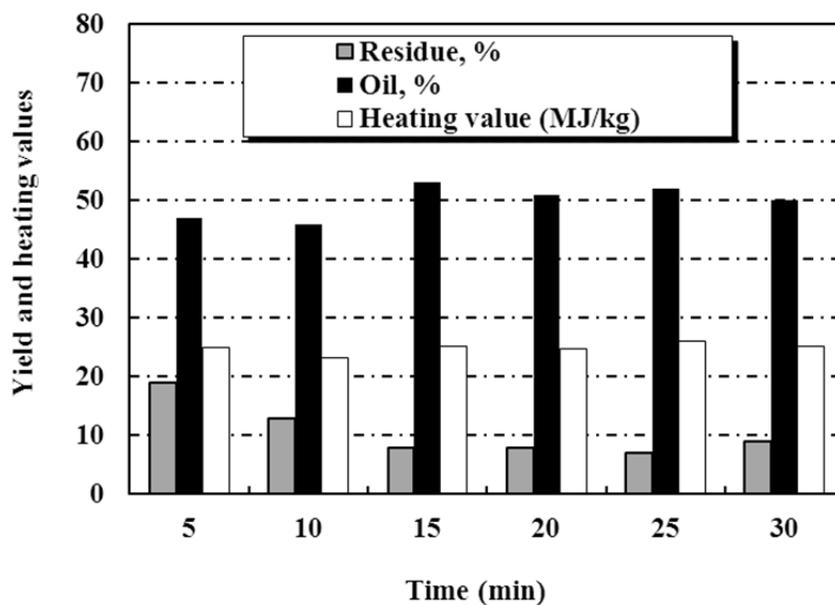


Figure 4.5 Effect of time on the yield and heating value of bio-oil and on the yield of residue (Initial N₂ pressure = 4 MPa, temperature = 280 °C and ethanol to water ratio = 50:50 and biomass to solvent ratio = 1:8 w/w).

4.2.4 Effect of biomass to solvent ratio

The effect of biomass to solvent ratio on the yield of bio-oil, residue and heating value was studied and the results are shown in Figure 4.6. Three biomass-to-solvent ratios (1:6, 1:8 and 1:10) were chosen for the study at the optimum predetermined conditions of temperature, ethanol to water ratio and time. It is obvious from the figure that increasing the ratio of solvent to biomass in the liquefaction process from 1:6 to 1:10 has very slight effect on both yield and heating value. However, decreasing the ratio of solvent to biomass from 1:8 to 1:6 resulted in an increase in the amount of residue from 8 to 14%. Similarly, increasing the ratio of solvent to biomass from 1:8 to 1:10 increased the residue content from 8 to 11%. Accordingly, applying 1:8 solvent to biomass ratio is favorable for this liquefaction system. According to previous results, the optimum

liquefaction conditions for giant miscanthus without catalyst were 280 °C, 50% ethanol, 15 min of time and 1:8 biomass to solvent ratio.

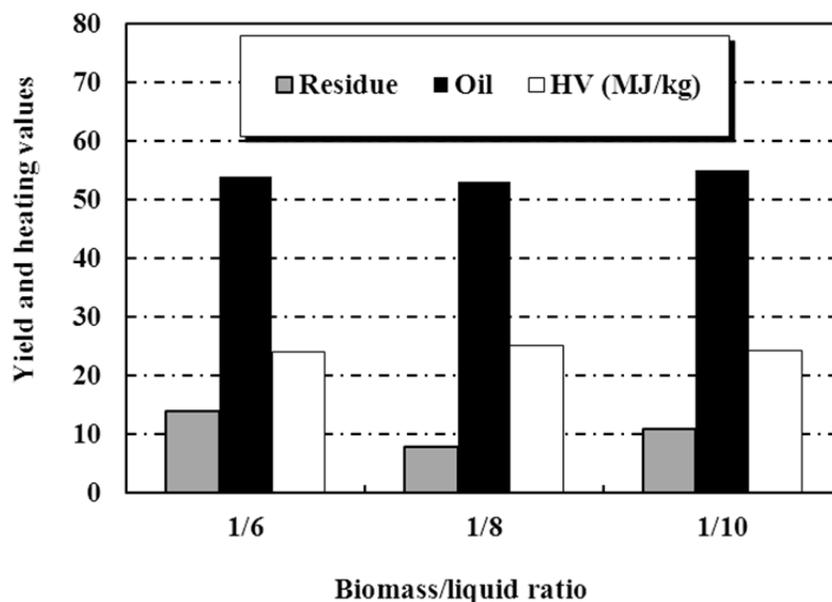


Figure 4.6 Effect of biomass to solvent ratios on the yield of bio-oil, residue yield and heating value (Initial N₂ pressure = 4 MPa, temperature = 280 °C, reaction time = 15 min and ethanol to water ratio = 50:50).

4.2.5 Effect of catalyst

As a trial to decrease the time of the liquefaction process and improve the heating value of the bio-oil, four different catalysts (formic acid-HCOOH, zinc chloride-ZnCl₂, trifluoroacetic acid (TFA)-CF₃COOH, and sodium carbonate-Na₂CO₃) were applied during the liquefaction of giant miscanthus. A low reaction time of 5 min was used for all experiments. Figure 4.7 shows the effect of the different catalysts on the yield of bio-oil and the amount of solid residue and the heating value of the produced bio-oil. It is clear from the figure that addition of these catalysts had almost no effect on the heating value

of the resultant bio-oil. However, the type of catalyst greatly affected the yield of crude bio-oil and the amount of solid residue. Zinc chloride produced the highest yield of bio-oil and the lowest amount of solid residues. On the other hand, sodium carbonate did not show the expected synergistic effect during the process, it produced the lowest yield of bio-oil and the highest amount of residues. Formic acid and trifluoroacetic acid produced results about midway between the previously mentioned two catalysts. These results indicate that comparable oil and residue and relatively good heating values can be produced with a reaction of short duration when an appropriate catalyst is applied.

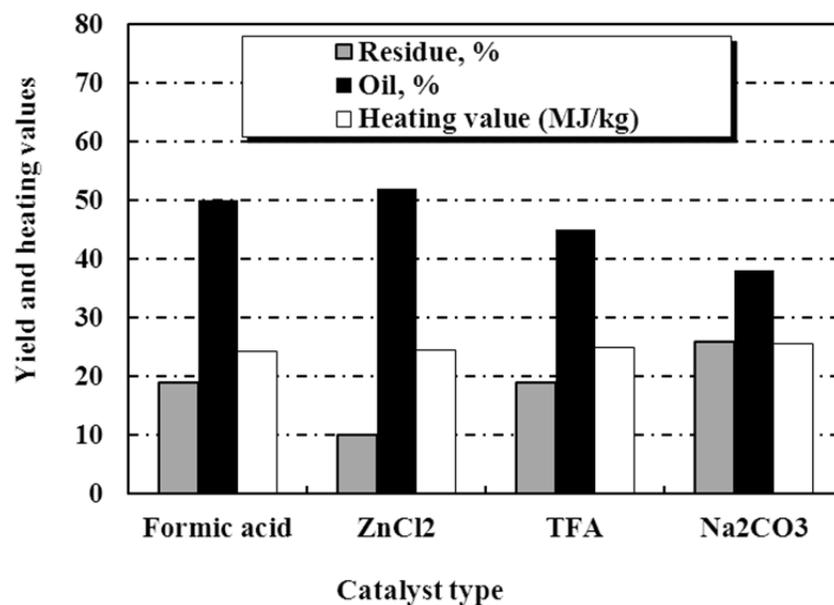


Figure 4.7 Effect of the different catalysts on the yield of bio-oil, amount of solid residue and the heating value (Initial N₂ pressure = 4 MPa, temperature = 280 °C, reaction time = 5 min and ethanol to water ratio = 50:50 and biomass to solvent ratio = 1:8 w/w).

4.2.6 GC-MS analysis

The identification of the major compounds in the crude bio-oil produced under the optimum conditions without catalysts and in the presence of four different catalysts is shown in Table 4.3.

Table 4.3 GC-MS identification of major components of crude bio-oil produced from liquefaction process with and without catalyst.

| RT | Compound Name | Area (%) | | | | |
|-------|--|-------------|---------------------------------|----------------------|-------|-------------------|
| | | No catalyst | Na ₂ CO ₃ | CF ₃ COOH | HCOOH | ZnCl ₂ |
| 2.38 | Acetic acid | 5.57 | 8.97 | 6.22 | | 2.88 |
| 4.86 | Acetic acid, hydroxy-, ethyl ester | 2.17 | - | 1.29 | 1.5 | 0.73 |
| 5.79 | Propanoic acid, 2-hydroxy-, ethyl ester | 7.56 | 1.67 | 3.49 | 4.18 | 11.43 |
| 6.31 | Furfural | 2.72 | - | 7.17 | 7.69 | 0.66 |
| 6.83 | Tricyclo[5.2.2.0(2,6)]undecan-11-one-8,9-dicarboxylic anhydride, 3-[(2-methoxyethoxy)methoxy]-2-methyl | - | - | 2.19 | 2.11 | - |
| 8.81 | Butanoic acid, 2-hydroxy-, ethyl ester | 1.48 | 1.59 | - | 0.8 | 0.87 |
| 10.62 | 2 furan methanol beta methoxy | - | - | 22.17 | 14.54 | 20.6 |
| 11.52 | phenol | 1.41 | 1.06 | - | - | 0.55 |
| 13.02 | 2-Cyclopenten-1-one, 2-hydroxy-3-methyl | 4.34 | - | 2.19 | 3.0 | - |
| 14.26 | Pentanoic acid, 4-oxo-, ethyl ester | 4.01 | 1.15 | 1.85 | 2.32 | 3.0 |
| 14.79 | Propanoic acid, 2-methyl-, anhydride | 2.53 | - | - | - | - |
| 15.07 | Phenol, 2-methoxy | 2.98 | 5.75 | 1.35 | | 1.22 |
| 17.61 | Phenol, 4-ethyl | 7.99 | 6.3 | 2.36 | 3.96 | 1.78 |
| 18.10 | Butanedioic acid, diethyl ester | 1.35 | - | - | - | - |
| 18.70 | 1,2-Benzenediol | 1.59 | 1.83 | 1.32 | 1.92 | - |
| 19.64 | 2-Furancarboxaldehyde, 5-(hydroxymethyl) | - | - | 3.33 | 5.75 | - |
| 20.53 | 1,2-Benzenediol, 4-methyl | 1.81 | - | - | - | - |
| 21.00 | Phenol, 4-ethyl-2-methoxy | 4.92 | 5.91 | 1.57 | 2.36 | 0.96 |
| 21.62 | 5-(Hydroxymethyl)-2-(dimethoxymethyl)furan | - | - | - | 13.54 | - |
| 22.43 | 3,3,3,6 tetramethoxy-1,4-cyclohexadiene | - | - | - | - | 21.08 |
| 22.93 | Butanoic acid, 3,3 dimethyl-2-(1-methyl) | 4.11 | - | - | - | - |
| 23.09 | Phenol, 2,6-dimethoxy | 4.54 | 8.27 | 1.71 | 1.84 | 1.72 |
| 24.42 | Vanillin | 1.95 | 1.73 | 1.58 | | 1.12 |
| 25.76 | Phenol, 2-methoxy-4-(1-propenyl) | 2.36 | 3.34 | - | - | - |
| 27.9 | 2-Propanone, 1-(4-hydroxy-3-methoxyphenyl) | - | 2.61 | - | - | - |
| 31.04 | Benzaldehyde, 4-hydroxy-3,5-dimethoxy | | 1.15 | 0.96 | 1.11 | 0.61 |
| 31.96 | phenol 2 6-dimethoxy-4-(2-propenyl) | 1.43 | - | - | - | - |
| 32.74 | Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl) | - | 2.18 | - | - | - |

It is obvious from the table that the bio-oil produced without catalyst contains high portions of phenolic compounds which lead to the instability of bio-oil and need to be converted through the upgrading process. The application of formic acid,

trifluoroacetic acid and zinc chloride catalysts lead to formation of high percentage of 2-furan methanol beta methoxy which is produced from decarbonilation of levoglucosan. Moreover, GC-MS analysis showed also that the crude bio-oil catalyzed by zinc chloride contained a high percentage of propanoic acid, 2-hydroxy-, ethyl ester, and 3,3,3,6 tetramethoxy-1,4-cyclohexadiene. The presence of these upgraded ester and olefin compounds confirm the result of principal component analysis (PCA) showing that the bio-oil produced by zinc chloride catalyst is completely different from other bio-oils. Acetic acid was at the highest levels when the reaction was catalyzed with sodium carbonate. Furan derivatives were mostly common in the formic acid catalyzed bio-oil analysis.

4.2.7 Principal component analysis

A multivariate data analysis was performed on the bio-oils produced by different catalysts using Unscrambler version 9.7 (CAMO, Corvallis, OR, USA). PCA was performed using five repetitions from GC-MS analysis data. As presented in Figure 4.8, PCA of GC-MS spectra showed a promising way to qualitatively classify different types of the bio-oil based on the catalyst type. The bio-oils produced without catalyst and with alkali sodium carbonate catalysts seem to have similar bio-oil compositions as they appear in one cluster. Similarly, bio-oils produced with two organic acids TFA and HCOOH appear in very close clusters and accordingly they might have comparable chemical composition. The bio-oil produced with solid zinc chloride catalyst exists in one cluster far away from other bio-oils and also seem to have completely different chemical composition. Accordingly, from these results, the type of catalyst have a pronounced effect on the chemical composition of bio-oils.

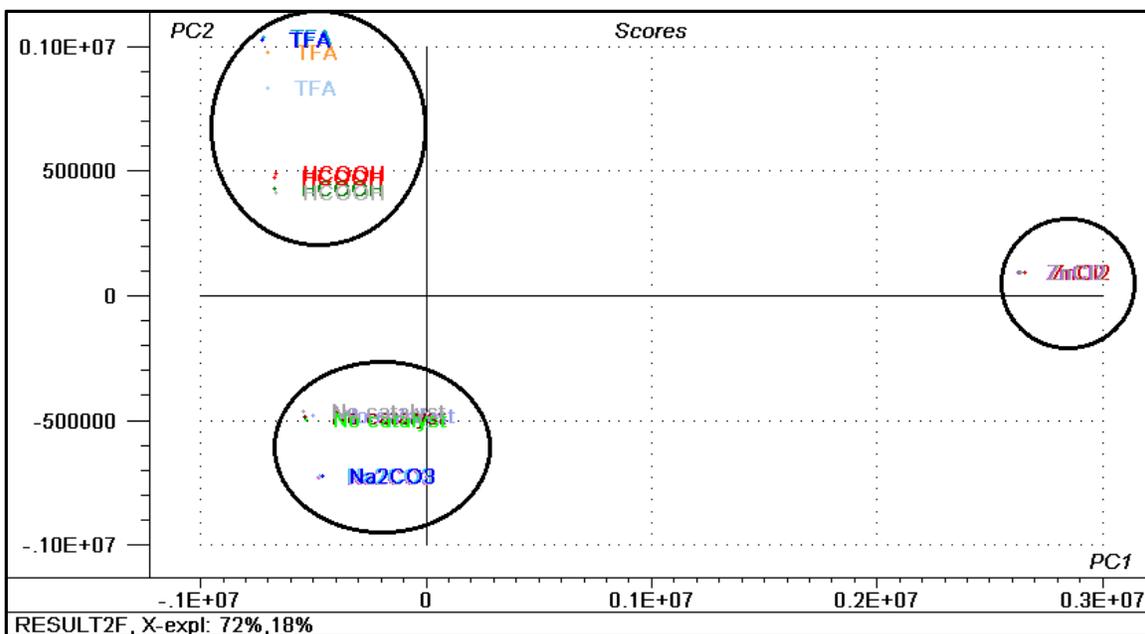


Figure 4.8 PCA for the bio-oils produced by different catalysts.

4.2.8 Heating value analysis

The crude bio-oil heating values were calculated for all bio-oils prepared in this study and the results are shown in Table 4.4. It is obvious that there is no specific trend for all temperatures and ethanol to water ratios combinations. Generally, the heating values for all non-upgraded bio-oils calculated in this study ranged between 22 and 26 MJ/Kg.

Table 4.4 Heating values of the produced bio-oil at different conditions.

| Temp°C | Ethanol to water ratio % | Catalyst | Time (min) | C % | H ₂ % | N ₂ % | O ₂ % | HV (MJ/Kg) |
|--------|--------------------------|---------------------------------|------------|-------|------------------|------------------|------------------|------------|
| 220 | 0 | Non | 30 | 59.70 | 6.32 | 0.34 | 33.64 | 23.81 |
| 220 | 10 | Non | 30 | 60.03 | 6.00 | 0.37 | 33.59 | 23.48 |
| 220 | 20 | Non | 30 | 59.22 | 6.21 | 0.33 | 34.24 | 23.40 |
| 220 | 30 | Non | 30 | 59.45 | 6.14 | 0.21 | 34.20 | 23.39 |
| 220 | 40 | Non | 30 | 60.65 | 6.47 | 0.00 | 32.88 | 24.46 |
| 220 | 50 | Non | 30 | 59.69 | 5.81 | 0.26 | 34.24 | 22.99 |
| 240 | 0 | Non | 30 | 61.05 | 6.28 | 0.28 | 32.39 | 24.40 |
| 240 | 10 | Non | 30 | 59.81 | 5.95 | 0.28 | 33.97 | 23.27 |
| 240 | 20 | Non | 30 | 61.95 | 6.01 | 0.61 | 31.44 | 24.46 |
| 240 | 30 | Non | 30 | 59.29 | 6.33 | 0.70 | 33.68 | 23.68 |
| 240 | 40 | Non | 30 | 59.84 | 6.24 | 0.19 | 33.74 | 23.73 |
| 240 | 50 | Non | 30 | 59.36 | 6.64 | 0.50 | 33.51 | 24.17 |
| 260 | 0 | Non | 30 | 58.40 | 6.55 | 0.59 | 34.46 | 23.58 |
| 260 | 10 | Non | 30 | 61.41 | 6.87 | 0.23 | 31.49 | 25.50 |
| 260 | 20 | Non | 30 | 60.49 | 6.37 | 0.35 | 32.79 | 24.28 |
| 260 | 30 | Non | 30 | 60.11 | 6.59 | 0.39 | 32.91 | 24.45 |
| 260 | 40 | Non | 30 | 58.08 | 6.37 | 0.55 | 35.00 | 23.13 |
| 260 | 50 | Non | 30 | 61.23 | 6.68 | 0.37 | 31.72 | 25.13 |
| 280 | 0 | Non | 30 | 57.38 | 6.68 | 0.00 | 35.94 | 23.19 |
| 280 | 10 | Non | 30 | 58.89 | 6.42 | 0.00 | 34.69 | 23.52 |
| 280 | 20 | Non | 30 | 57.89 | 7.91 | 0.43 | 33.78 | 25.45 |
| 280 | 30 | Non | 30 | 61.86 | 7.10 | 0.63 | 30.41 | 26.14 |
| 280 | 40 | Non | 30 | 62.76 | 6.61 | 0.00 | 30.62 | 25.72 |
| 280 | 50 | Non | 30 | 60.47 | 6.99 | 0.04 | 32.50 | 25.20 |
| 280 | 50 | Non | 5 | 61.57 | 6.53 | 0.31 | 31.59 | 25.05 |
| 280 | 50 | Non | 10 | 62.03 | 5.18 | 0.62 | 32.17 | 23.20 |
| 280 | 50 | Non | 15 | 61.54 | 6.63 | 0.45 | 31.38 | 25.22 |
| 280 | 50 | Non | 20 | 61.67 | 6.32 | 0.22 | 31.79 | 24.76 |
| 280 | 50 | Non | 25 | 62.88 | 6.78 | 0.17 | 30.18 | 26.07 |
| 280 | 50 | Non | 30 | 60.47 | 6.99 | 0.04 | 32.50 | 25.20 |
| 280 | 50(1:6) | Non | 15 | 58.18 | 7.04 | 0.26 | 34.52 | 24.19 |
| 280 | 50(1:8) | Non | 15 | 61.54 | 6.63 | 0.45 | 31.38 | 25.22 |
| 280 | 50(1:10) | Non | 15 | 59.25 | 6.75 | 0.21 | 33.79 | 24.25 |
| 280 | 50 | HCOOH | 5 | 59.43 | 6.77 | 0.51 | 33.29 | 24.42 |
| 280 | 50 | ZnCl ₂ | 5 | 60.35 | 6.63 | 0.35 | 32.67 | 24.62 |
| 280 | 50 | CF ₃ COOH | 5 | 61.01 | 6.67 | 0.39 | 31.93 | 25.01 |
| 280 | 50 | Na ₂ CO ₃ | 5 | 60.67 | 7.18 | 0.80 | 31.35 | 25.71 |

4.3 Esterification upgrading of crude bio-oil

The produced bio-oil at the optimum liquefaction conditions (temperature = 280 °C, ethanol to water ratio = 50:50, time = 15 min, biomass to solvent ratio = 1:8, and with no catalyst) was upgraded by the application of zeolite catalysts. The presence of ethanol

in the supercritical states helped in applying lower temperature during the process when compared to other upgrading processes which use very high temperature in order to perform the upgrading reactions for the crude bio-oil. A batch from bio-oil was prepared and two different solid acid zeolite catalysts (zeolite Y CBV400 and ZSM-5) were applied for esterification and upgrading of the bio-oil. The conditions used for upgrading bio-oil were given previously in section 3.5.

Table 4.5 and Table 4.6 show the GC-MS identification for the major chemical compounds in the crude and upgraded bio-oil produced by upgrading with the two types of zeolite. The chemical composition of the bio-oils were classified into groups and represented in Figure 4.9. It is clear from both tables and the figure that the presence of ethanol in the bio-oil during the upgrading processes enhanced the esterification reactions for the bio-oil. The major organic acids exist in the crude bio-oil (acetic acid and butanoic acid, 3, 3 dimethyl-2-(1-methyl) were significantly decreased and converted into different esters. The percentage of esters increased from 22.78% in the crude bio-oil to 51.06% and 32.12% in the bio-oils upgraded with zeolite Y CBV400 and zeolite ZSM-5 respectively. Phenolic compounds were also significantly decreased in the upgraded bio-oil. The percentage of phenolic compounds was decreased from 32.42% in the crude bio-oil to 4.33% and 6.92% in the upgraded bio-oils. Aldehydes and ketones were converted also through acetalization reactions and the amount of ketones was decreased from 11.17% in the crude bio-oil to 3.26% and 6.08% in the upgraded bio-oils. Application of both zeolite catalysts in the upgrading step also resulted in the formation of many saturated and unsaturated hydrocarbons. The percentage of alkanes was significantly increased from 2.11% in the crude bio-oil to 25.83% and 40.0% in the bio-oils upgraded

with zeolite Y CBV400 and ZSM-5 respectively. About 6.65% of alkenes compounds were also formed when zeolite Y CBV 400 was used as a catalyst. It seems that zeolite ZSM-5 is more specific for the formation of alkanes while zeolite Y CBV 400 tends to form both alkanes and alkenes. These changes in the chemical composition of upgraded bio-oil increased the stability of bio-oil during storage because of the reduction of oxygen content in the upgraded bio-oil and the transformation of acids, aldehydes, ketones and phenolic compounds into more stable compounds. Accordingly, the upgrading of bio-oil was successfully performed at relatively low temperature (280 °C) using zeolite catalysts.

Table 4.5 GC-MS identification for the major compounds in the crude bio-oil

| Compound Name | Area (%) |
|---|--------------|
| Esters | |
| Acetic acid, hydroxy-, ethyl ester | 2.17 |
| Propanoic acid, 2-hydroxy-, ethyl ester | 7.56 |
| Butanoic acid, 2-hydroxy-, ethyl ester | 1.48 |
| Pentanoic acid, 4-oxo-, ethyl ester | 4.01 |
| Butanedioic acid, diethyl ester | 1.49 |
| Octanoic acid, 7-oxo-, methyl ester | 1.33 |
| 2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester | 1.23 |
| Eicosanoic acid, ethyl ester | 1.50 |
| Hexanedioic acid, bis (2-ethylhexyl) ester | 2.01 |
| Total esters | 22.78 |
| Acids | |
| Acetic acid | 5.57 |
| Butanoic acid, 3,3 dimethyl-2-(1-methyl) | 4.11 |
| Total acids | 9.68 |
| Phenols | |
| Phenol | 1.41 |
| Phenol, 2-methoxy | 2.98 |
| Phenol, 4-ethyl | 7.99 |
| 1,2-Benzenediol | 1.59 |
| 1,2-Benzenediol, 4-methyl | 1.81 |
| Phenol, 4-ethyl-2-methoxy | 4.92 |
| Phenol, 2,6-dimethoxy | 4.54 |
| Vanillin | 1.95 |
| Phenol, 2-methoxy-4-(1-propenyl)-, (E) | 2.36 |
| Phenol, 4-(2-methylpropyl) | 1.44 |
| Phenol, 2,6-dimethoxy-4-(2-propenyl) | 1.43 |
| Total phenols | 32.42 |
| Ketones | |
| 1,2-Cyclopentanedione, 3-methyl | 4.34 |
| 2-Pentanone, 5,5-diethoxy | 1.56 |
| 3-Nonanone, 2-methyl | 1.42 |
| Tridecanone | 1.15 |
| Ethanone, 1-(2,5 dihydroxyphenyl) | 1.47 |
| Ethanone, 1-(4-hydroxy-3-methoxyphenyl) | 1.23 |
| Total ketones | 11.17 |
| Aldehydes | |
| Furfural | 2.72 |
| Alkanes | |
| Propane, 2-methoxy-2-methyl | 2.11 |
| Alcohols | |
| 2-Pentanol, 3-methyl | 2.18 |
| 2-furanethanol, beta-methoxy (S) | 1.47 |
| 2-Furanmethanol, tetrahydro-, acetate | 2.74 |
| Total alcohols | 6.39 |
| Heterocyclic | |
| 1,3-Dioxolane,4-ethyl-4-methyl-2-pentadecyl | 1.48 |

Table 4.6 GC-MS identification of major compounds of the upgraded crude bio-oil using two types of zeolite

| Zeolite Y CBV400 Catalyst | | Zeolite ZSM-5 catalyst | |
|--|--------------|--|--------------|
| Compound | Area % | Compound | Area% |
| <u>Acids</u> | | | |
| Propanoic acid, 2-methyl | 1.14 | | |
| <u>Esters</u> | | <u>Esters</u> | |
| Propanoic acid, ethyl ester | 6.05 | Acetic acid, hydroxy-, ethyl ester | 0.74 |
| Pentanoic acid, 2-hydroxy-4-methyl, methyl ester | 3.83 | Propanoic acid, 2-hydroxy-, ethyl ester | 7.08 |
| Butanoic acid, ethyl ester | 0.98 | Propanoic acid, 3-methoxy, methyl ester | 1.08 |
| Propanoic acid, 2-hydroxy-, ethyl ester, (S) | 4.75 | Butanoic acid, 2-hydroxy-, ethyl ester | 1.51 |
| Propanoic acid, 2-methyl, heptyl ester | 1.29 | Acetic acid, ethoxy-, ethyl ester | 4.52 |
| Butanoic acid, 2-hydroxy-, ethyl ester | 1.64 | Methoxyacetic acid, cyclohexyl ester | 0.6 |
| Acetic acid, ethoxy-, ethyl ester | 5.57 | 2-Furancarboxylic acid, ethyl ester | 1.01 |
| Propanoic acid, 2-hydroxy-ethyl ester | 12.07 | Pentanoic acid, 4-oxo-, ethyl ester | 6.78 |
| Methoxyacetic acid, cyclohexyl ester | 1.01 | Pentanoic acid, 2-methyl-4-oxo-, ethyl ester | 1.58 |
| Hexanoic acid, 2-pentenyl ester, (Z) | 1.13 | Hexanoic acid, 5-oxo-, ethyl ester | 0.95 |
| Pentanoic acid, 4-oxo-, ethyl ester | 6.26 | Butanedioic acid, diethyl ester | 2.79 |
| Butanedioic acid, diethyl ester | 2.09 | Pentanedioic acid, diethyl ester | 1.73 |
| Cyclopentanecarboxylic acid, pentyl ester | 1.33 | Hexanedioic acid, diethyl ester | 0.9 |
| Pentanedioic acid, diethyl ester | 1.42 | Hexadecanoic acid, ethyl ester | 0.85 |
| Hexadecanoic acid, ethyl ester | 1.64 | | |
| Total Esters | 51.06 | Total Esters | 32.12 |
| <u>Phenols</u> | | <u>Phenols</u> | |
| Phenol, 2-ethyl | 1.45 | Phenol | 0.67 |
| Phenol, 4-ethyl-2-methoxy | 1.63 | Phenol, 2-methoxy | 1.31 |
| 2,5-Diethylphenol | 1.25 | Phenol, 4-ethyl- | 2.66 |
| Total Phenols | 4.33 | Phenol, 4-ethyl-2-methoxy | 1.52 |
| <u>Ketones</u> | | 2,5-Diethylphenol | 0.76 |
| Cyclopentanone, 2-methyl | 1.47 | Total Phenols | 6.92 |
| Ethanone, 1-(2-methyl-1-cyclopenten-1-yl) | 0.92 | <u>Ketones</u> | |
| 2,5-Cyclohexadien-1-one,4-ethyl-3,4-dimethyl | 0.87 | 2-Butanone, 3-hydroxy- | 1.28 |
| Total Ketones | 3.26 | 2-Cyclopenten-1-one, 2-methyl | 1.05 |
| <u>Alkanes</u> | | 2,5-Hexanedione | 0.88 |
| Ethane, 1-ethoxy-1-methoxy | 5.04 | 2(3H)-Furanone, dihydro-5-methyl | 0.98 |
| Propane, 1,1-dimethoxy-2-methyl | 14.38 | 2-Cyclopenten-1-one, 2,3-dimethyl | 1.89 |
| Butane, 2-ethoxy-2-methyl | 2.16 | Total Ketones | 6.08 |
| Octane, 2-methyl- | 0.80 | <u>Alkanes</u> | |
| Ethane, 1-bromo-1,2-diethoxy | 3.45 | Ethane, 1-ethoxy-1-methoxy | 33.6 |
| Total Alkanes | 25.83 | Propane, 2-ethoxy | 1.11 |
| <u>Alkenes</u> | | Propane, 1,1-dimethoxy-2-methyl | 2.68 |
| 2-Butene, 1,1-dimethoxy | 1.31 | Pentane, 1-methoxy | 1.26 |
| 4-Ethyl-4-methyl-1-hexene | 1.13 | Ethane, 1-ethoxy-1-methoxy | 1.35 |
| 2-Butene, 1,1-dimethoxy | 2.59 | Total Alkanes | 40.0 |
| 1-Octene, 7-methyl | 0.79 | <u>Alcohols</u> | |
| Methylcycloheptene | 0.83 | 2-Hexanol, 5-methyl | 0.67 |
| Total Alkenes | 6.65 | 3-heptanol | 1.45 |
| <u>Alcohols</u> | | 3-Buten-2-ol, 2-methyl | 1.18 |
| 2-Furanmethanol, tetrahydro | 1.05 | Total Alcohols | 3.3 |
| <u>Heterocyclic</u> | | <u>Heterocyclic</u> | |
| Dioxolane | 0.75 | 2-Methoxy-1,3-dioxolane | 7.72 |

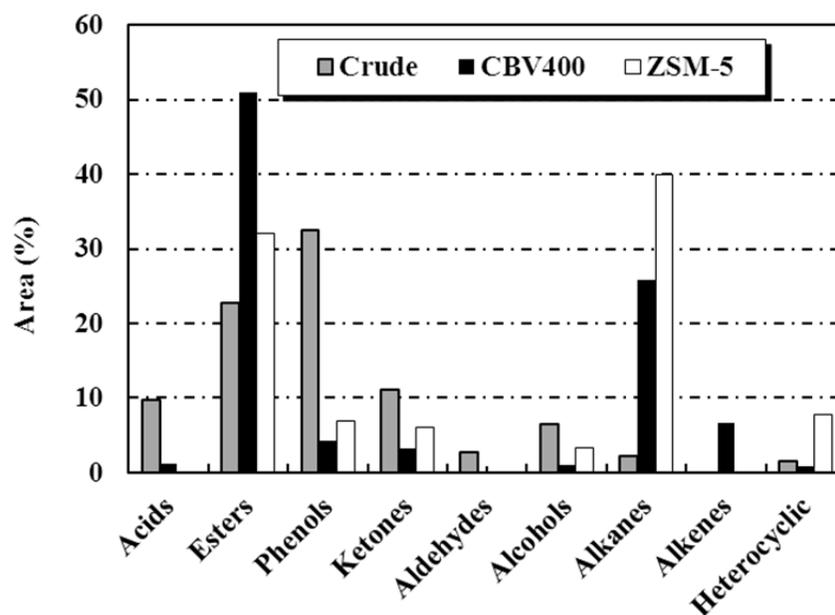


Figure 4.9 Area% of the major organic compounds in the crude and upgraded bio-oil with the two types of zeolite

Heating value analysis of the upgraded bio-oil by the two different types of zeolite was determined and compared with the heating value of crude bio-oil. It was found that the heating value for upgraded bio-oil was slightly higher than for crude bio-oil. The heating value for the upgraded bio-oil by zeolite Y CBV400 and ZSM-5 catalysts was 28.3 and 27.4 MJ/Kg, respectively, compared with 25.2 MJ/Kg for the crude bio-oil.

4.3.1 FTIR spectra

Figure 4.10 shows the FTIR spectra representing functional groups compositional analysis for crude bio-oil and the two upgraded bio-oils. The broad absorbance band between 3200 and 3600 cm^{-1} are ascribed to $\nu(\text{O-H})$ vibrations of hydroxyl groups which indicate the presence of alcohols, phenols and water in the bio-oil (Hassan et al., 2009). This peak was broader in case of crude bio-oil indicating more water, alcohols and

phenolic compounds. The presence of the O–H absorbance peak together with the presence of C=O stretching vibrations between 1680 and 1720 cm^{-1} indicates the presence of carboxylic acids and ester compounds. This C=O peak was more pronounced in case of upgraded bio-oils because of the presence of high amount of ester compounds observed from the GC-MS. The strong absorbance peak of C–H stretching vibrations between 2800 and 3000 cm^{-1} and the C–H deformation vibrations at 1380 cm^{-1} in the upgraded bio-oils indicates the presence of methyl and methylene groups of alkanes. The presence of alkenes in the upgraded bio-oils was indicated by the absorbance of stretching vibration of C=C peaks between 1650 and 1600 cm^{-1} ; this absorbance peak is also indicative for aromatics. Absorbance peaks between 800–900 cm^{-1} may be related to out-of-plane C–H bending of mono, polycyclic and substituted aromatic groups (Gercel, 2002). The peaks between 950 and 1300 cm^{-1} are due to the presence of primary, secondary and tertiary alcohols (Das et al., 2004); these peaks were more pronounced in the case of upgraded bio-oil. It is obvious that FTIR spectra confirm the results obtained by GC-MS analysis and indicating the presence of more alkanes, alkenes and ester compounds in the upgraded bio-oils.

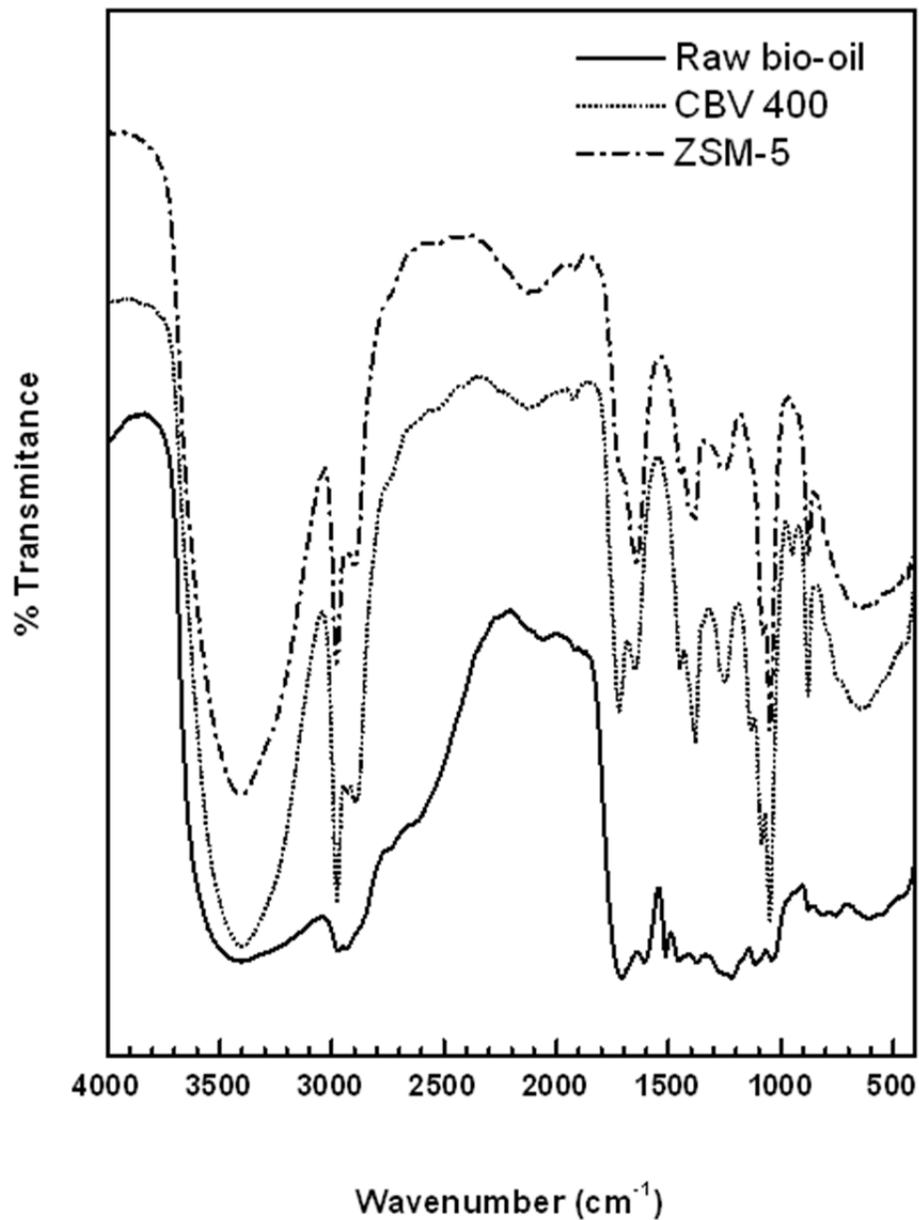


Figure 4.10 FTIR spectra for crude and upgraded bio-oils by zeolite catalysts.

4.4 One step liquefaction and upgrading of biomass

In a new study in the thermochemical conversion of biomass into liquid fuels, a set of experiments were conducted to investigate the liquefaction of biomass and the

upgrading of the produced bio-oil in one step. Experiments were conducted using two different catalysts (zeolite Y CBV 400 and aluminum silicate) and their combinations with zinc chloride at a temperature of 280 °C, initial hydrogen pressure of 1 MPa, residence time of 1 h and a co-solvent of 80% ethanol and 20% water. The results of GC-MS analysis for the crude bio-oil without catalyst and the four different upgraded bio-oils are shown in Tables 4.7, 4.8 and Figure 4.11.

It is obvious from both tables and the figure that the chemical composition of bio-oil (without catalyst) and aluminum silicate upgraded bio-oil were comparable. The percentages of acidic compounds in both bio-oils was very high (11.38 and 10.19%) compared to other bio-oils. The amount of ester compounds in both bio-oils obtained with and without catalyst was comparable and ranged from 32.57 to 37.83%. Phenolic compounds were reduced in the catalyzed experiments compared to results of the non-catalyzed experiment. Zeolite Y CBV400 and zinc chloride had the lowest amount of phenols; however, the highest amount of phenolic compounds was obtained when aluminum silicate was applied. The same trend was obtained also in the ketones, the lowest amount was obtained when the combination of zeolite Y CBV400 and zinc chloride was used, the aluminum silicate and non-catalyzed reactions had the highest amount of ketones. In contrast to previous results, alcohols were obtained at a high level of 11.60% when the zeolite was used. A relatively high amount of alcohols was obtained when the combination of aluminum silicate and zinc chloride and when no catalyst was added. The lowest amount of alcohols was 1.72% which was obtained when the combination of zeolite Y CBV400 and zinc chloride was used. Alkanes were obtained at high levels of 14.57% when the zeolite alone was used; a yield of 3.87% was obtained

when the combination of zeolite Y CBV400 and zinc chloride was applied. Heterocyclic compounds appeared only when zinc chloride was added to the two types of catalysts.

From these results, it is important to combine the zinc chloride with the two types of catalyst, it played a major role in the hydrolysis reactions of the biomass in the earlier stages of the reaction in the presence of water. Thus, using ethanol alone might be less effective because the presence of water with zinc chloride leads to formation of hydrochloric acid which is important for breaking down the raw biomass at the beginning of the reaction. Zeolite Y CBV400 with the zinc chloride had relatively the best results for one step liquefaction and upgrading of biomass. Based on the results of this study, the methods employed to both produce and upgrade bio-oil are good approach in the conversion of biomass processes when compared with conventional liquefaction and upgrading methods which require very high temperatures and energy inputs for a long reaction time. However, more experiments need to be conducted in the future in order to study the effect of other parameters such as reaction time, amount of alcohol, amount of catalysts, other types of catalysts, etc.

Table 4.7 GC-MS identification of major compounds in the bio-oil without catalyst

| Compound Name | Area % |
|---|---------------|
| Acids | |
| Propanoic acid, 2hydroxy | 3.35 |
| Propanoic acid, 2-methyl-, anhydride | 6.57 |
| Dehydroacetic Acid | 1.46 |
| Total acids | 11.38 |
| Esters | |
| Acetic acid, hydroxy-, ethyl ester | 3.78 |
| Propanoic acid, 2-hydroxy-, ethyl ester | 1.99 |
| Propanoic acid, 2-hydroxy-, ethyl ester, (S) | 7.61 |
| Butanoic acid, 2-hydroxy-, ethyl ester | 2.48 |
| Acetic acid, ethoxy-, ethyl ester | 0.99 |
| 2-Furancarboxylic acid, ethyl ester | 1.02 |
| Pentanoic acid, 4-oxo-, ethyl ester | 3.53 |
| Pentanoic acid, 2-methyl-4-oxo-, ethyl ester | 0.90 |
| Butanedioic acid, diethyl ester | 1.06 |
| Butanedioic acid, diethyl ester | 4.48 |
| Butanoic acid, 2 octyl ester | 1.60 |
| Pentanedioic acid, diethyl ester | 1.30 |
| Hexanethioic acid, S-decyl ester | 1.06 |
| Benzenepropanoic acid, 4-hydroxy-, methyl ester | 2.51 |
| Hexadecanoic acid, ethyl ester | 2.24 |
| Hexadecanoic acid, 1,1-dimethylethyl ester | 1.19 |
| Total esters | 37.74 |
| Phenols | |
| Phenol, 2-methoxy | 2.73 |
| Phenol, 4-ethyl | 10.15 |
| Phenol, 2-methoxy-4-methyl | 1.74 |
| Phenol, 4-ethyl-2-methoxy | 5.81 |
| Phenol, 2,6-dimethoxy | 3.54 |
| Phenol, 2-methoxy-4-propyl | 2.29 |
| 4-Propyl-1,1'-diphenyl | 2.30 |
| Total phenols | 28.56 |
| Ketones | |
| 2 Propanone, 1-methoxy | 2.17 |
| 2(5H)-Furanone, 5,5-dimethyl | 5.51 |
| 2-Cyclopenten-1-one, 2-hydroxy-3-methyl | 1.86 |
| Total ketones | 9.54 |
| Alcohols | |
| Isopropyl Alcohol | 1.54 |
| 3-Heptanol | 1.48 |
| 4-Ethyl-4-heptanol | 2.41 |
| Homovanillyl alcohol | 1.07 |
| Total alcohols | 6.5 |
| Heterocyclic | |
| 1,3-Dioxolane, 2,2-diethyl | 1.86 |

Table 4.8 GC-MS identification of major compounds in the bio-oils in presence of different catalysts

| Compound name | Area % | | | |
|--|-------------------|-------------------------------------|------------------|------------------------------------|
| | Aluminum silicate | Aluminum silicate and zinc chloride | Zeolite Y CBV400 | Zeolite Y CBV400 and zinc chloride |
| <u>Acids</u> | | | | |
| Acetic acid | | | | |
| Propanoic acid, 2hydroxy | 5.02 | - | - | - |
| Propanoic acid, 2-methyl-, anhydride | 5.17 | - | - | - |
| Total acids | 10.19 | - | - | - |
| <u>Esters</u> | | | | |
| Acetic acid, hydroxy-, ethyl ester | 4.19 | 2.47 | 1.36 | 1.32 |
| Propanoic acid, 2-hydroxy-, ethyl ester | 9.04 | 18.72 | 16.09 | 17.71 |
| Propanoic acid, 2-hydroxy-, ethyl ester, (S) | | | | |
| Butanoic acid, 2-hydroxy-, ethyl ester | 2.40 | 2.19 | 2.88 | 2.17 |
| Acetic acid, ethoxy-, ethyl ester | 1.73 | 1.42 | 0.78 | 1.24 |
| 2-Furancarboxylic acid, ethyl ester | 1.35 | 1.11 | - | - |
| Pentanoic acid, 4-oxo-, ethyl ester | 4.13 | 4.56 | 9.37 | 8.80 |
| Pentanoic acid, 2-methyl-4-oxo-, ethyl ester | | | | |
| Butanedioic acid, diethyl ester | 2.49 | 1.88 | 1.31 | 2.89 |
| Butanoic acid, 2 octyl ester | | | | |
| Pentanedioic acid, diethyl ester | 1.25 | 1.70 | - | - |
| Butanoic acid, 3,3-dimethyl-2-(1-methylethyl)-, methyl ester | 4.09 | - | - | - |
| 2-Propylidene-malonic acid, diethyl ester | - | - | - | 1.56 |
| 2,4-Hexadienedioic acid, 3-methyl-4-propyl-, dimethyl ester | 2.62 | - | - | - |
| Cyclohexadien-4-one-1-propionic acid, methyl ester | 2.55 | - | - | - |
| Benzenepropanoic acid, 4-hydroxy-, methyl ester | - | 0.76 | - | - |
| Hexanoic acid, 2-tetrahydrofurylmethyl ester | | | | 2.14 |
| Hexadecanoic acid, ethyl ester | 1.36 | 2.17 | 0.78 | - |
| Total esters | 37.20 | 36.98 | 32.57 | 37.83 |
| <u>Phenols</u> | | | | |
| Phenol | - | 1.28 | - | - |
| Phenol, 2-methoxy | 2.73 | 4.13 | 1.54 | 2.76 |
| Phenol, 4-ethyl | 9.96 | 5.45 | 7.32 | 6.06 |
| Phenol, 2-methoxy-4-methyl | 1.38 | 0.86 | 0.89 | |
| Phenol, 4-ethyl-2-methoxy | 5.85 | 3.61 | 4.23 | 3.26 |
| Phenol, 2,6-dimethoxy | 3.32 | 3.70 | 1.15 | 1.12 |
| Phenol, 2-methoxy-4-propyl | 1.83 | 1.05 | 1.73 | 1.26 |
| Total phenols | 25.07 | 20.08 | 16.86 | 14.46 |
| <u>Ketones</u> | | | | |
| 2-Cyclopenten-1-one, 2-methyl- | 1.32 | 1.11 | - | - |
| 2 Propanone, 1-methoxy | | - | | - |
| 2,5-Hexanedione | 0.83 | - | 1.21 | - |
| 2(5H)-Furanone, 5,5-dimethyl | 6.34 | 4.08 | 4.57 | 4.40 |
| 3,6-Heptanedione | - | - | 1.23 | 1.49 |
| 1,2-Cyclopentanedione, 3-methyl | 2.04 | - | 1.25 | - |
| 3-Hexanone, 2-methyl | 1.13 | - | - | - |
| 1,3-Dioxolan-4-one, 2-(1,1-dimethyl ethyl) | - | 1.66 | - | |

Table 4.8 (continued)

| | | | | |
|--|--------------|-------------|--------------|-------------|
| Total ketones | 11.66 | 6.85 | 8.26 | 5.89 |
| <u>Alcohols</u> | | | | |
| Isopropyl Alcohol | - | 1.34 | - | 1.72 |
| 2,4-Pentanediol | - | 2.23 | 6.98 | - |
| 2-Furanmethanol, tetrahydro-, acetate | - | 1.72 | 3.30 | - |
| 3-Heptanol | - | - | 1.32 | - |
| Total alcohols | - | 5.29 | 11.60 | 1.72 |
| <u>Alkanes</u> | | | | |
| Ethane, 1-ethoxy-1-methoxy | - | - | 9.67 | 3.53 |
| Ethane, 1,2-diethoxy | - | 1.31 | - | - |
| Propane, 1,1-dimethoxy-2-methyl | - | - | - | 1.26 |
| Butane, 1-methoxy | - | - | 3.61 | 2.61 |
| Butane, 1,1'-[methylenebis(oxy)]bis[3-methyl | - | - | 1.29 | - |
| 2-Ethoxypentane | 1.88 | - | - | - |
| Total alkanes | 1.88 | 1.31 | 14.57 | 7.4 |
| <u>Heterocyclic</u> | | | | |
| 1,3-dioxolane,4-methyl-2-pentyl | - | 1.26 | - | - |
| 1,3-Dioxolane, 2-ethyl-4-methyl | - | 2.50 | - | 2.00 |
| Total heterocyclic | - | 3.76 | - | 2.00 |

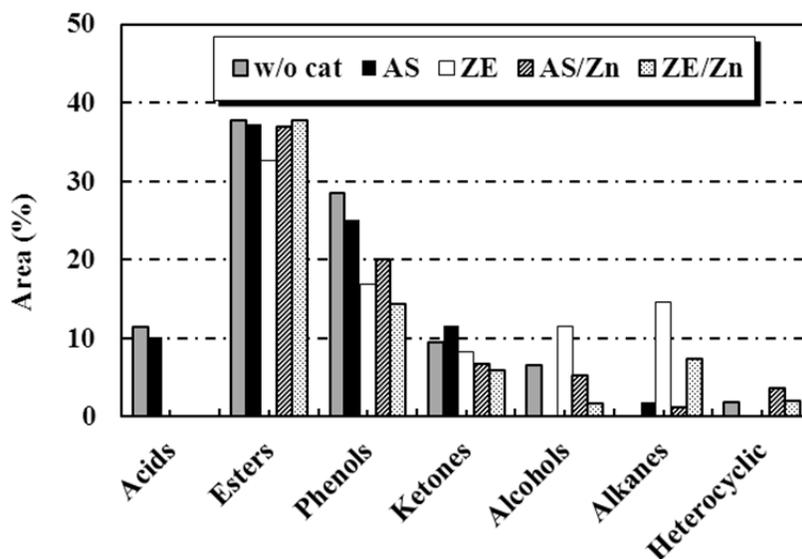


Figure 4.11 Representation of different compounds in the one step liquefaction and upgrading of biomass using various catalysts (w/o cat = without catalyst, AS = aluminum silicate, ZE = zeolite Y CBV 400, AS/Zn = aluminum silicate and zinc chloride and ZE/Zn = zeolite and zinc chloride).

Heating values for the catalyzed reactions were comparable and ranging between 28 MJ/Kg, however, in the non-catalyzed reaction, heating value was not as high as catalyzed experiments. The heating value for non-catalyzed reaction was 21.19 MJ/Kg, while the maximum heating value obtained when the combination of aluminum silicate and zinc chloride were used was 28.69 MJ/Kg. Figure 4.12 shows the differences between heating values for the catalyzed and non-catalyzed experiments.

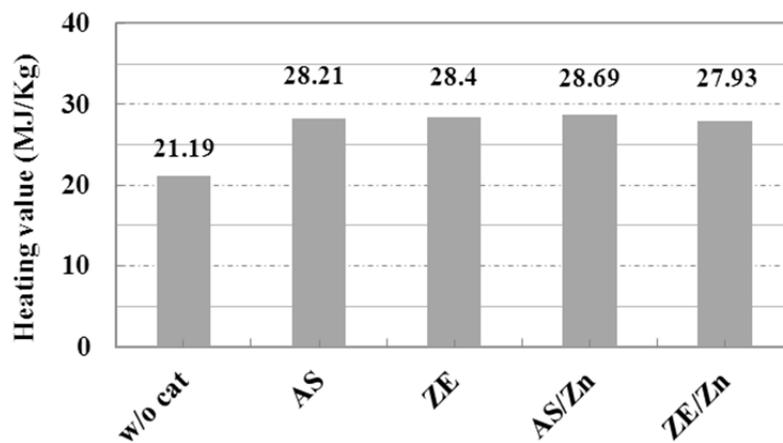


Figure 4.12 Heating values for non-catalyzed and catalyzed experiments of one liquefaction and upgrading step (w/o cat = without catalyst, AS = aluminum silicate, ZE = zeolite Y CBV 400, AS/Zn = aluminum silicate and zinc chloride and ZE/Zn = zeolite and zinc chloride).

CHAPTER V

SUMMARY

In this study the liquefaction of giant miscanthus biomass into bio-oil was studied. The effect of various parameters such as; temperature, ethanol to water ratio, time, biomass to solvent ratio and the catalyst were examined. The effect of temperature and ethanol to water ratio was studied by making combinations with the four temperatures and the six ethanol to water ratios. From the obtained results, the optimum combination of temperature and ethanol to water ratio was at 280 °C and 50:50 respectively. Experiments were conducted firstly at 30 min of residence time, however, later on when the effect of time was studied, a high yield of crude bio-oil and a low solid residue amount was obtained at a time of 15 min. Best result was obtained at a biomass to solvent ratio of 1:8, the higher and lower ratios did not give the desired results. The effect of catalyst was studied using four types of catalysts. The results were greatly improved; a 90% conversion of biomass with 52% yield of bio-oil were obtained at only 5 min. which means a significant improvement by comparing to the previous work when more time and higher temperatures were used. Difference between heating values for all the experiments was not large, heating values ranged between 22 and 26 MJ/Kg. GC-MS identification for major compounds for the produced bio-oil at the optimum conditions without catalyst and with the addition were performed. The bio-oils produced without catalyst and with alkali sodium carbonate catalysts seem to have similar bio-oil

compositions according to PCA study. Similarly, bio-oils produced with two organic acids (TFA and HCOOH) appear in very close clusters and accordingly they might have comparable chemical composition. The bio-oil produced with solid zinc chloride catalyst exists in one cluster far away from other bio-oils and also seem to have completely different chemical composition.

Two methods of upgrading were performed. First one was the conventional upgrading of crude bio-oil and the second method was a new approach of the one step liquefaction and upgrading of raw biomass. In the conventional upgrading, two types of zeolite were chosen for the experiments. Acids, phenolic compounds, aldehydes and ketones were greatly reduced in the upgraded bio-oil. On the other hand, esters and alkanes were increased in the upgraded bio-oil than those in the crude bio-oil. From these results, it can be concluded that the amount of oxygen was greatly reduced in the upgraded samples and accordingly the stability of bio-oil was increased due to the reduction in the compounds which cause the instability of bio-oil such as aldehydes, ketones and phenolic compounds.

The new approach of upgrading was performed using four types of catalysts and catalyst combinations. Co-solvent of ethanol and water was used for the experiments. The presence of water and zinc chloride was essential to effectively breakdown the high molecular weight polymers of biomass. Results showed that the raw biomass was effectively converted with high amount of esters and alkanes and less amounts of acids, ketones, and phenolic compounds. More experiments need to be performed to study the effects of other parameters.

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