



Faculty of Resource Science and Technology

Upgrading of Wood Waste Bio-oil via Transesterification

Noraziani binti Lot (21822)

Bachelor of Science with Honours

(Resource Chemistry)

2011

## **ACKNOWLEDGEMENT**

First of all, I would like to thank Allah that I was able to finished and complete this research within the arranged time. Not to forget, a special thanks to my supervisor, Madam Rafeah Wahi for her guidance during this two semesters. She has been a great help to me by providing a lot of information and guidelines for this research. Besides that, I would also like to send my gratitude to Assoc Prof Dr. Zainab Ngaini whose been giving a new idea regarding the method and also provide the reagent and equipment for the research.

To the laboratory assistance, Tuan Haji Karni, technician, Mr. Rajuna Tahir and Mr. Ismadi, I would like to thanked them for their kind assistance. They always come in handy when I faced difficulties in my research. Also to the laboratory staff at GCMS laboratory, Mr. Benedict for his help in analyzed the samples. Besides that, I would also like to thank Sharifah Mona, master student that always guide during the research.

To my mother, Faridah Dollah, thanks a lot mom, for your support either mentally or financially. Lastly, not to forget, my precious friends Calidya Idem, Cynthia Rudy, Julia and Vannessa Lawai whose share the same laboratory, thanks for always there accompanied me during the overtime on weekend. Thanks a lot girl.

## **DECLARATION**

I hereby declare that no portion of the work referred to this thesis has been submitted in support of an application for another degree or qualification to this or any other university or institution of higher learning.

---

**(NORAZIANI BINTI LOT)**

Date:

## TABLE OF CONTENTS

Acknowledgement .....	I
Declaration .....	II
Table of Contents .....	III
List of Abbreviations .....	V
List of Tables and Figures .....	VI
ABSTRACT .....	1
CHAPTER 1	
INTRODUCTION	
1.1 Background of Study .....	2
1.2 Problem Statement .....	4
1.3 Research Objectives .....	4
CHAPTER 2	
LITERATURE REVIEW	
2.1 Bio-oil .....	5
2.2 Biomass .....	6
2.3 Chemical Structure and Major Components of Biomass .....	7
2.4 Properties of Biomass .....	8
2.5 Bio-oil Upgrading Techniques .....	11
2.5.1 Homogeneous Acid-catalyzed Transesterification .....	11
2.5.2 Base-catalyzed Transesterification .....	12
2.5.3 Alkali-catalyzed Transesterification .....	13
2.5.4 Transesterification using Solid-Acid Catalysts .....	13
2.6 Role of Catalyst in Transesterification .....	14
2.7 Role of Solvent in Transesterification .....	15

## CHAPTER 3

### MATERIALS AND METHODS

3.1 Material .....	16
3.2 Microwave Pyrolysis .....	16
3.3 Removal of Water and Dichloromethane (DCM) .....	17
3.4 Heterogeneous Transesterification .....	17
3.4.1 Weight Ratio of Methanol to Bio-oil .....	18
3.4.2 System Work up .....	19
3.5 Bio-oil Characterization .....	19
3.6 Wood Waste Characterization .....	20
3.6.1 Moisture Content .....	20
3.6.2 Ash Content .....	21

## CHAPTER 4

### RESULTS AND DISCUSSIONS

4.1 Main Properties of Bio-oil .....	23
4.2 Fourier Transform Infrared Spectrometer (FTIR) Analysis .....	26
4.3 Gas Chromatography Mass Spectrometer (GCMS) Analysis .....	31
4.4 Wood Waste Characterization .....	40
4.5 Effect of Methanol/Bio-oil Ratio on Transesterification .....	40

## CHAPTER 5

CONCLUSION .....	41
REFERENCES .....	43
APPENDICES .....	58

## LIST OF ABBREVIATIONS

EFB	Empty fruit bunch
DCM	Dichloromethane
FFA	Free fatty acid
FTIR	Fourier transforms infrared
GCMS	Gas chromatography mass spectrometer
GCV	Gross calorific value
HHV	Higher heating value
LHV	Lower heating value
NaOH	Sodium hydroxide
CaO	Calcium oxide
R	Ratio
MJ/kg	Megajoule per kilogram
Wt.%	Weight percentages

## LIST OF TABLES

Table 4.1	Physical properties of bio-oil	23
Table 4.2	The main functional groups determine by FTIR analysis	27
Table 4.3	Area percentage (%) of chemical compounds in bio-oils	32
Table 4.4	Area percentage (%) of the main compounds in the raw bio-oil	33
Table 4.5	Area percentage (%) of the main compounds in upgraded bio-oil (R=2:1)	35
Table 4.6	Area percentage (%) of the main compounds in the upgraded bio-oil (R=1:1)	37
Table 4.7	Proximate analysis data of wood waste	42

## LIST OF FIGURES

Figure 3.1	Flow chart of transesterification reaction	18
Figure 3.2	Flow chart of the experiment of wood waste conversion to fuel material	22
Figure 4.1	Samples of (a) upgraded bio-oil (R=2:1), (b) upgraded bio-oil (R=1:1) and (c) raw bio-oil diluted in DCM	25
Figure 4.2	Samples of (a) raw bio-oil, (b) upgraded bio-oil (R=1:1) and (c) upgraded bio-oil (R=2:1)	26
Figure 4.3	FTIR Spectra of raw bio-oil	30
Figure 4.4	FTIR Spectra of upgraded bio-oil (R=1:1)	28
Figure 4.5	FTIR Spectra of upgraded bio-oil (R=2:1)	29
Figure 4.3	Gas chromatogram of raw bio-oil	53
Figure 4.4	Gas chromatogram of upgraded bio-oil (R=2:1)	54
Figure 4.5	Gas chromatogram of upgraded bio-oil (R=1:1)	55

## Upgrading of Wood Wastes Bio-oil via Transesterification

Noraziani bt. Lot

Resource Chemistry Programme, Faculty of Resource Science and Technology,  
University Malaysia Sarawak

### ABSTRACT

Depletion of fossil fuels leads to a research to find an alternative source to replace it. Esterification and transesterification are the most widely used upgrading method to produce biofuels with similar properties as petroleum fuels. This study attempted to improve the bio-oil properties produced from microwave pyrolysis by using heterogeneous transesterification reaction with calcium oxide (CaO) as catalyst. The objectives of this study are to improve the pyrolytic bio-oils properties and to determine the ideal weight ratio of methanol/bio-oil for transesterification reaction. Dried sample of wood waste is subjected to microwave pyrolysis to produce pyrolytic bio-oil. The bio-oil is then upgraded using transesterification reaction with the aid of CaO and carried out in two different weight ratio of methanol/bio-oil. Characterization of the bio-oil before and after transesterification reaction shows that the properties of bio-oil are successfully improved. Gross calorific values of upgraded bio-oil are 32.949 and 34.483 MJ/kg. Based on the experimentations, ideal weight ratio of methanol/bio-oil is 2:1 which greatly improved certain bio-oil properties. In conclusion, although this weight ratio improves certain properties of bio-oil the most important properties of bio-oil which is calorific value are reduced significantly.

**Key words:** Bio-oil, transesterification, pyrolysis, ester

### ABSTRAK

*Kekurangan minyak fosil menyebabkan para penyelidik menganalisa sumber baru yang sesuai bagi menggantikannya. Antara kaedah yang sering digunakan untuk menghasilkan minyak bermutu tinggi yang mempunyai sifat-sifat yang hamper sama dengan minyak petrol adalah kaedah pengesteran dan transesterifikasi. Dalam kajian sifat-sifat minyak yang terhasil daripada prose pyrolysis dengan menggunakan reaksi transesterifikasi campuran dengan menggunakan kalsium oksida (CaO) sebagai pemangkin. Objektif kajian ini adalah untuk meningkatkan kualiti minyak dan untuk menentukan nisbah berat metanol/minyak yang terbaik. Sampel kayu kering diproses menggunakan kaedah pyrolysis untuk menghasilkan minyak pyrolitik. Kemudian, minyak yang terhasil tadi ditransesterifikasi dengan bantuan CaO sebagai pemangkin dan dijalankan dalam dua nisbah berat metanol/minyak yang berlainan. Analisis sifat minyak sebelum dan selepas transesterifikasi menunjukkan sifat-sifat minyak telah berjaya diperbaiki. Jumlah kalori minyak yang telah diperbaiki adalah 32.949 dan 34.483 MJ/kg. berdasarkan eksperimen, nisbah berat yang sesuai ialah 2:1 yang menunjukkan peningkatan yang tinggi kepada sifat-sifat tertentu minyak. Kesimpulannya, walaupun nisbah tersebut berjaya memingkatkan kualiti minyak tetapi jumlah kalori minyak yang merupakan sifat terpenting minyak berkurang.*

*Kata kunci: Minyak, transesterifikasi, pirolisis, ester*

# CHAPTER 1

## INTRODUCTION

### 1.1 Background of Study

Over the past few years the level of interest placed on biomass as an alternative fuel source has greatly increased. Thus, many researches on the method for converting those waste into biofuels have been develop. A very promising method of converting biomass to energy is through thermo-chemical conversion, more particularly, pyrolysis. Pyrolysis is carried out within a temperature range of 300-600°C, in the absence of oxygen, typically in a nitrogen atmosphere. Biomass pyrolysis results in the production of three products, namely, gas, bio-oil and bio-char. The relative proportion of these products depends very much on the pyrolysis method, the characteristics of the biomass and the reaction parameters. A very high heating rate, along with rapidly quenching the reaction is required in order to maximize the liquid yields. This can potentially yield up to 75% bio-oil (Ringer *et al.*, 2006; Crofcheck, 2007).

Bio-oils are dark brown liquid produced from pyrolysis process and composed of very complex mixture of oxygenated hydrocarbon with significant proportion of water from both original moisture and reaction product. However, these type of oils obtained from this process which can be called fast pyrolysis process cannot be used as transportation fuels without prior upgrading process. This is due to their high oxygen content (35-40 wt % dry basis) and water content (15-25 wt %) (Ringer *et al.*, 2006; Crofcheck, 2007). Thus, the bio-oil product must go through upgrading process such as transesterification reaction for instance, homogeneous acid catalyzed transesterification, base-catalyzed transesterification, alkaline transesterification and transesterification using solid-acid catalysts.

Homogeneous acid catalyst can simultaneously catalyze both esterification and transesterification. Previous studies by Zhang (2003a, 2003b), have shown that the acid catalyzed biodiesel production can be economically compete with base catalyzed process especially when low cost feedstock is used. However, this reaction takes longer time which is about 4000 times slower than homogeneous base catalyzed reaction (Srivastava & Prasad, 2000). Base-catalyzed transesterification is the second stage of biodiesel synthesis which gives high conversion of methyl ester up to 98% as stated by Yusup and Khan (2010). However, this reaction is very sensitive to the purity of the reactant as free fatty acid (FFA) content must be in a certain limit (Sharma *et al.*, 2008). As for alkaline transesterification, maximum conversion efficiency was recorded at 0.5% of NaOH as reported by Ramadhas *et al.* (2005). However, the amount of catalyst used for alkaline transesterification should be ranged between 0.3 - 1.0%. Excess amount of catalyst leads to formation of emulsion that reduced the conversion efficiency. Transesterification using solid-acid catalysts have more significant advantages compared to the conventional homogeneous acids due to less corrosion, less toxicity and less environmental problems (Lou *et al.*, 2008). However, the use of those solid acids usually requires high reaction temperature, long reaction time and relatively high pressure (Zhang *et al.*, 2010).

In this study, heterogeneous catalyzed transesterification was used due to higher tolerance to water and FFA in oils and ability to simultaneously catalyze both the esterification and transesterification reactions. According to Yan *et al.* (2009) some salts and oxides of magnesium, calcium, and zinc are active in transesterification. Recently, the reaction of some crude oils into biodiesel can be directly catalyzed by calcium oxide (CaO) catalyst when water content in the oils is less than 2 (wt%) and FFA content less than 3.5 (wt%) (Yan *et al.*, 2009).

## 1.2 Problem Statement

The reducing sources of fuel due to depletion of the fossil fuels lead to the research on a renewable and environmentally acceptable fuel sources. From the previous research, the agricultural waste can be used as another alternatives source to replace fossil fuels, by using thermochemical conversion processes such as microwave pyrolysis.

However, the bio-oil produced is not ready to be used as a biodiesel due to their high oxygen content (35-40 wt% dry basis) and water content (15-25 wt%) (Czernik *et al.*, 2002). Besides that, the low calorific value and high density of the bio-oil also did not fit the requirements properties. Thus, the upgrading process must be done in order to achieve a high quality of bio-oil by heterogeneous catalyzed transesterification. This method is used due to the high tolerance to water and FFA in oils and can catalyzed both esterification and transesterification reactions. CaO is an active catalyst in transesterification reaction and able to directly catalyzed the reaction of crude oils into biodiesel (Yan *et al.*, 2009).

## 1.3 Research Objectives

This study will focus on the use of transesterification process to produce a bio-oil of improved quality. The specific objectives of this study are to:

- To upgrade the bio-oil produced from pyrolysis in order to improve its properties
- To determine ideal weight ratio of methanol/bio-oil that can be used in transesterification reaction.

## CHAPTER 2

### LITERATURE REVIEW

#### 2.1 Bio-oils

Bio-oils are dark brown, free-flowing organic liquids that are comprised of highly oxygenated compounds (Mohan *et al.*, 2006). Bio-oils include pyrolysis oils, pyrolysis liquids, bio-crude oil (BCO), wood liquids, wood oil, and wood distillates.

Rapid and simultaneous depolymerizing and fragmenting cellulose, hemicelluloses, and lignin with rapid increase in temperature produced pyrolysis liquids. Bio-oils have unusual attributes which due to the presence of many reactive species. Chemically, bio-oil is a complex mixture of water, guaiacols, catecols, syringols, vanilins, furancarboxaldehydes, isoeugenol, pyrones, acetic acid, formic acid, and other carboxylic acids (Mohan *et al.*, 2006). Other major groups of compound including hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids and phenolics are also presence in bio-oil. Continuous phase of bio-oil is an aqueous solution of hoo cellulose decomposition products and small molecules from lignin decomposition which allowed bio-oil to be considered as a microemulsion (Mohan *et al.*, 2006). Pyrolytic lignin macromolecule leads to a discontinuous phase that required the continuous liquid phase to stabilize them. These microemulsion stabilization is achieved by hydrogen bonding and nanomicelle and micromicelle formation (Mohan *et al.*, 2006). Therefore, the exact chemical nature of each bio-oil is dependant on the feedstock and the pyrolysis variables.

## 2.2 Biomass

Biomass is biological material derived from living, or recently living organisms. In terms of biomass for energy, it is defined as plant based material, but biomass can equally apply to both animal and vegetable derived material (“What is Biomass?”, 2011). It consists mainly of carbon and is composed of a mixture of organic molecules containing hydrogen, including atoms of oxygen, nitrogen and a small quantity of other atoms such as alkali, alkaline earth and heavy metals (“What is Biomass?”, 2011).

Despite containing low content of carbon, biomass has small content of sulfur, nitrogen and ash which leads to lower emission of SO<sub>2</sub>, NO<sub>x</sub> and soot than that of conventional fossil fuels (Zhang *et al.*, 2007). In addition, zero emission of CO<sub>2</sub> can be achieved due to release of CO<sub>2</sub> from biomass into the plants by the process of photosynthesis (Zhang *et al.*, 2007). Therefore, biomass has been considered as a great alternative fuel source over the past few years.

Method that is commonly used to convert biomass to energy is thermo-chemical conversion called pyrolysis. Pyrolysis is carried out within a temperature range of 300-600°C in inert conditions, typically in a nitrogen atmosphere (Zhang *et al.*, 2007). However, complex mixtures of organic compounds in pyrolysis oils can exhibit a wide spectrum of chemical functionality and contain some water. Thus, direct use as fuels might face some difficulties due to their high viscosity, poor heating value, corrosiveness and instability which require upgrading techniques to improve their characteristics (Junming *et al.*, 2008).

### 2.3 Chemical Structure and Major Components of Biomass

The chemical structure and major components of biomass are important for producing derived fuels and chemicals. There are three major components of biomass, namely, cellulose, hemicelluloses and lignin (Yaman, 2004). Cellulose is generally the largest fraction which consists about 40-50% of the biomass weight followed by hemicelluloses, 20-40% and the smallest fraction is lignin which exists in about 10-20% of the material by weight (McKendry, 2002).

Cellulose is a glucose polymer which contains linear chains of (1,4)-D-glucopyranose units and linked in 1-4 in the  $\beta$ -configuration. The average molecular weight is around 100 000 (McKendry, 2002). Cellulose is insoluble in water due to the formation of the skeletal structure of most biomass and cell wall material (Yaman, 2004).

Hemicellulose is a mixture of polysaccharides which composed mostly of sugars such as glucose, mannose, xylose and arabinose and methylglucuronic and galaturonic acids with average molecular weight less than 30 000 (McKendry, 2002). It differs from cellulose as it consist of heterogeneous branched polysaccharide that bind tightly to the surface of each cellulose microfibril (McKendry, 2002).

Lignis are highly branched, substituted, mononuclear aromatic polymers in the cell walls of woody species which can form a lignocellulosic complex by reacting to the adjacent cellulose fibers (Yaman, 2004).

Pyrolysis of these three components of biomass shows that hemicelluloses had a higher CO<sub>2</sub> yield while cellulose record higher yield of CO and lignin produced high yield of H<sub>2</sub> and CH<sub>4</sub> respectively (Gaojin *et al.*, 2010). The pyrolysis decomposition of all biomass occurred in the

temperature range of 250-400°C. Lignin is the first components decompose which occurred at the lowest temperature and continues up to the temperature around 900°C. Hemicellulose and cellulose decompose over the temperature range of 160-360°C and 240-390°C, respectively (°Camvuka *et al.*, 2003).

## **2.4 Properties of Biomass**

### **Ash Content**

Ash contents in biomass are due to the present of minerals in the structure of trees and shrubs in addition to any soil contamination. Characterization of ash by elemental composition and fusion temperatures indicates the softening and melting behavior of ash which is important characteristic in biomass fuels selection as it provides information on amount of ash production (Hubbard *et al.*, 2007). The presence of ash in the bio-oil can cause erosion, corrosion, and gumming problems in the engine valves by affecting the power plants (Monti *et al.*, 2007). The ash content of the bio-oils from microwave pyrolysis is 0.04 wt%. Problems associated with ash content become more serious when the ash content of the fuel is greater than 0.1 wt% (Yu *et al.*, 2007).

### **pH**

Most bio-oils have a pH in the range of 2.0-3.8 due to the presence of organic acids, mostly acetic and formic acid. The acids in the bio-oils are corrosive to common construction materials

such as carbon steel and aluminum, especially with elevated temperature and with the increase in water content. However, bio-oils are noncorrosive to stainless steels (Yu, *et al.*, 2007).

### **Moisture Content**

Thermal conversion requires low moisture content feedstock, usually less than 50%, while bio-conversion can use high moisture content feedstocks (McKendry, 2002). Feedstocks with high moisture content can also be use in thermal conversion but it will result in adversely impact on the overall energy balance (McKendry, 2002). Thus, the most efficient biomass sources for thermal conversion to biofuels are woody and low moisture content herbaceous plant species (Yu *et al.*,2007).

### **Calorific Value**

The calorific value is define as an expression of the energy content, or heat value that released when burnt in the air (McKendry, 2002). It is the most important properties required for biofuels which determine the energy value of the fuels. There are three forms of the calorific value can be expressed which are, the gross calorific value (GCV), higher heating value (HHV), and the nett calorific value (NCV) which known as lower heating value (LHV) (McKendry, 2002).

The HHV represents the maximum amount of energy potentially recoverable from biomass source. It is the total energy content released when the fuel is burnt in air including the latent heat contained in the water vapour. The actual amount of energy recovered is different for each conversion technology. Therefore, the latent heat contained in the water vapour cannot be used

effectively in the practical term which makes the suitable value to use for the energy available for the subsequent use is LHV (McKendry, 2002).

Bio-oils have a lower gross heating value than petroleum fuels and will therefore require an increased fuel flow to compensate the combustion in a firebox. The heating value of the bio-oils from microwave pyrolysis is approx 41.7% of a petroleum fuel oil. In other words, 2.4 kg of the bio-oil is required to provide the same energy as 1.0 kg of petroleum oil (Yu, *et al.*, 2007, p.962).

### **Water Content**

There are two source of water in bio-oil which is the moisture in the raw sample and the water produced as a result of the dehydration reactions occurring during the pyrolysis. Therefore, depending on the feedstock and process conditions, water content can differ in a wide range (15-30%). At this concentration water is usually miscible with the oligo-cellulosic derived components because of the solubilizing effect of other polar hydrophilic compounds (low-molecular-weight acids, alcohols, hydroxyaldehydes, and ketones) mostly originating from the decomposition of carbohydrates. The presence of water has both negative and positive effects on the oil properties. Obviously, it lowers its heating value, contributes to the increase in ignition delay, and the decrease in combustion rate compared with engine fuels. On the other hand, it improves bio-oil flow characteristics (reduces the oil viscosity), which is beneficial to combustion (Yu *et al.*, 2007).

## **Viscosity**

One of the main problems associated with biofuels conversion is high viscosity of biomass which can give rise to the formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristic (Chakrabarti & Ahmad, 2008). Therefore, in order to be considered as a fuel, the bio-oils must meet certain viscosity standard. The viscosity of fuel oils is usually around 2.5-30 mm<sup>2</sup>/s at 40°C. The kinematic viscosity of the bio-oils was difficult to determine because the level of the bio-oils in the viscometer could not be read easily. Therefore, the dynamic viscosity was measured. Blending with organic solvent such as methanol and ethanol can reduce viscosity (Yu, *et al.*, 2007).

## **2.5 Bio-oil Upgrading Techniques**

### **2.5.1 Homogeneous Acid-catalyzed Transesterification**

Homogeneous acid-catalyzed transesterification is a process that uses liquid acid catalyst replacing liquid base-catalyzed transesterification. Acid catalysts that are commonly used in this reaction are sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and hydrochloric acid (HCl) (Lam *et al.*, 2010). This reaction is better than that of base-catalyzed process due to its insensitivity to the presence of FFAs in the feedstock (Kulkarni & Dalai, 2006) and ability to catalyze both esterification and transesterification simultaneously (Jacobson *et al.*, 2008).

In previous study, it was reported that acid catalyst is more efficient when the amount of FFA in the oil exceeds 1wt.% (Zhang *et al.*, 2003a; Canakci & Van Gerpen, 1999; Freedmen *et al.*, 1984). Besides that, the acid-catalyzed biodiesel production can be economically compete

with respect to base-catalyzed process using virgin oils, especially when the low-cost feedstocks was used (Zhang *et al.*, 2003a, 2003b). There are two factors that must be considered during this process which is molar ratio of alcohol/bio-oils and concentration of alcohol. It is stated that the increase in molar ratio results in increasing on ester conversion and faster conversion at high alcohol concentration (Canakci & Van Gerpen, 1999). However, this reaction takes longer time which is about 4000 times slower than homogeneous base catalyzed reaction (Srivastava & Prasad, 2000).

### **2.5.2 Base-catalyzed Transesterification**

Base-catalyzed transesterification is the second stage of biodiesel synthesis which gives high conversion of methyl ester up to 98% as stated by Yusup and Khan (2010). Optimum condition required for this reaction are temperature of 55 °C with methanol/oil molar ratio of 8/1 and potassium hydroxide as catalyst at 2% (ww-1). The conversion of methyl esters recorded exceeded 98% after 5h and has a product quality that match to biodiesel with international standards (Yusup & Khan, 2010). However, this reaction is very sensitive to the purity of the reactant as free fatty acid (FFA) content must be in a certain limit (Sharma *et al.*, 2008).

The base strength of catalysts affect greatly on their catalytic activities in transesterification reaction as the increasing of base strength leads to higher conversion of methyl ester. For instance, the conversion of methyl ester by faujasite zeolites was higher than that of parent zeolites due to more electropositive cations which increase the base strength of faujasite zeolites (Philippou *et al.*, 2000).

### **2.5.3 Alkali-catalyzed Transesterification**

Alkali-catalyzed transesterification is a reaction which uses alkali catalyst instead of acid or base catalyst. Common catalysts used in alkali-catalyzed transesterification are sodium hydroxide and potassium hydroxide. Although this method is the most popular process for biodiesel production, strict feedstock specification is still required. Only highly refined vegetable oils should be used as feedstock to produce biodiesel by this method. Furthermore, the water and free fatty acid (FFA) contents in the reaction system should be less than 0.1 and 0.5%, respectively. High water contents might lead to low yield of biodiesel due to the hydrolysis which will become the dominant reaction.

Maximum conversion efficiency of alkaline transesterification was recorded at 0.5% of NaOH as reported by Ramadhas *et al.* (2005) which concluded that high amount of catalyst increase the yield of biodiesel. However, excess amount of catalyst leads to formation of emulsion that reduced the conversion efficiency. Thus, the amount of catalyst used for alkaline transesterification should be ranged between 0.3 - 1.0%.

### **2.5.4 Transesterification using Solid-Acid Catalysts**

Solid acid catalysts have more significant advantages compared to the conventional homogeneous acids due to less corrosion, less toxicity and less environmental problems (Lou *et al.*, 2008). However, the use of those solid acids usually requires high reaction temperature, long reaction time and relatively high pressure (Zhang *et al.*, 2010). Thus, further researches are

necessary to solve these problems. Recently, a lot of work has been carried out in relation to solid acid as catalysts for esterification reaction. In recent study, ferric sulfate shows a high catalytic activity when used as a solid acid catalyst to catalyze the esterification of FFA in waste cooking oil (WCO). In addition, ferric sulfate has a lower price and could be easily recovered due to its very lower solubility in oil which makes it suitable to be used as the potential catalyst.

## **2.6 Role of Catalyst in Transesterification**

The types of conventional catalysts used in transesterification reaction are depending upon the nature of the oil used for production of biodiesel. The choices of acid and alkali catalysts depend on the free fatty acids (FFA) content in the raw oil. There are certain amount of FFA should not exceed for transesterification to occur by an alkali catalyst (Zhang *et al.*, 2010). Catalysts used for the transesterification of triglycerides are divided into three classes which are known as alkali, acid and base catalysts.

Alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective compared to other catalysts (Ma & Hanna, 1999). Sodium hydroxide or potassium hydroxide has been used as a catalyst in the process of alkaline methanolysis, both in concentration from 0.4 to 2% wt of oil (Tomasevic & Marinkovic, 2003). Refined and crude oils use base catalyst such as sodium hydroxide or potassium hydroxide with 1wt.% resulted in successful conversion (Tomasevic & Marinkovic, 2003). Previous study done by Yan *et al.* (2009) used heterogeneous zinc and lanthanum mixed oxides as catalyst which varied in molar ratio. From the study, molar ratio of 3:1 of zinc to lanthanum showed the highest activity in oil transesterification.

## 2.7 Role of Solvent in Transesterification

The type of the alcohol used in the transesterification process does not affect the yield of biodiesel produce. The selection of the alcohol is based on the cost and performance of the alcohol itself (Sharma *et al.*, 2008). Methanol and ethanol are frequently used in both laboratory research and in biodiesel industry (Demirbas, 2003; Fukuda *et al.*, 2001). However, due to low cost and high reactivity of methanol makes it the first choice for the transesterification reaction (Zhang *et al.*, 2010). In addition, experiment by Nye *et al.* (1983) suggests that the initial reagent phase miscibility plays an important role in base-catalyzed transesterification. Phase miscibility can be affected by two factors which are hydrophobicity and reaction temperature applied in the reaction (Nye *et al.*, 1983). Large molecular weight alcohol increased the value of hydrophobicity in the reaction and the increasing of molecular weight also increased the reaction temperature as more energy is required for the conversion to occur (Liu, 1994).

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Material

Wood sample was obtained from local saw mills in Sematan, Sarawak. It was firstly washed in order to remove impurities followed by sun drying to remove moisture. The sample then will be reduced in size range less than 1-5 mm (Ringer *et al.*, 2006) by using grinder. The sample is then stored in an airtight container at room temperature for the pyrolysis process.

#### 3.2 Microwave Pyrolysis

The wood sample was sun dried so that the sample will contain only about 5-10% of moisture. Then, approximately 10g of the dried sample was placed in a microwave (input power 1000 W, frequency of 2.45MHz and nitrogen flow of 500ml/min). The quartz containing sample was placed in the microwave and tighten using parafilms. The microwave was warmed up and the nitrogen gas flows for 30 min before continue with pyrolysis in order to prepared inert condition. The sample was taken out after 10 min. The bio-oils produced was collected using DCM, stored in vials sealed with parafilm and placed in refrigerator.