Development of Potential Biodiesel from Agricultural Wastes

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DECLARATION

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

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ABSTRACT

Biomass in the form of agricultural waste is believed to have potential in producing biodiesel. In this project, palm oil mill effluent (POME) wastes were used. The wastes were obtained from the cooling pond of Bau Palm Oil Mill (BAPOM), Sarawak. The wastes were undergoing transesterification in the presence of methanol and catalysts. Two types of catalysts were introduced which are heterogeneous and homogeneous base catalysts. The use of homogeneous base catalyst made the POME biodiesel existed in flakes-form and difficult to be purified. The percentages yield is 2.2% by weight. However, biodiesel which used heterogeneous base catalyst were produced in liquid-form and easy to be purified. The percentages yield is 23% by weight. The biodiesel were analyzed using several tests such as Fourier Transform Infrared (FTIR) Spectrometer, Gas Chromatography Mass Spectrometer (GC-MS) as well as physical tests like odour, viscosity and colour. From the analysis, it is proved that the biodiesel from POME had some fuel properties such as low acidity, viscosity and water content. Thus, it has the potential to become one of the energy sources in substituting diesel.

Keyword: *heterogeneous, homogeneous, biodiesel, wastes, transesterification*

ABSTRAK

Biomas dalam bentuk sisa pertanian dipercayai mempunyai potensi untuk menghasilkan biodiesel. Sisa buangan kilang kelapa sawit digunakan dalam projek ini. Sisa tersebut diperolehi daripada kolam penyejukan di Bau Palm Oil Mill (BAPOM), Sarawak. Sisa tersebut telah menjalani proses transesterifikasi dengan kehadiran metanol dan katalis. Dua jenis katalis telah digunakan iaitu katalis bes heterogen dan homogen. Penggunaan katalis bes homogen membuatkan biodiesel POME terhasil dalam bentuk kepingan dan sukar untuk ditulenkan. Peratusan hasil beratnya ialah 2.2%. Walaubagaimanapun, biodiesel yang menggunakan katalis bes heterogen terhasil dalam bentuk cecair dan mudah untuk ditulenkan. Peratusan hasil beratnya ialah 23%. Biodiesel dianalisis dengan menggunakan beberapa ujian seperti spectrometer Fourier Transform Infrared (FTIR), Gas Chromatography Mass Spectrometer (GC-MS) dan ujian fizikal seperti bau, kelikatan dan warna. Berdasarkan analisis, dapat dibuktikan bahawa biodiesel POME mempunyai beberapa ciri-ciri bahan bakar seperti rendah asid, kurang likat dan rendah kandungan air. Oleh yang demikian, ia berpotensi untuk menjadi salah satu daripada sumber tenaga bagi menggantikan diesel.

Kata kunci: *heterogen, homogen, biodiesel, sisa, transesterifikasi*

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LIST OF ABBREVIATIONS

FT-IR	Fourier Transform-Infra Red Spectrometry
GC-MS	Gas Chromatography-Mass Spectrometry
SALCRA	Sarawak Land Consolidation & Rehabilitation Authority
EFB	Empty Fruit Bunch
FFA	Free Fatty Acid
POME	Palm Oil Mill Effluent
CaO	Calcium Oxide
NaOH	Sodium Hydroxide

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Due to the increase in population, urbanization as well as living standard, people seem to be very demanding for petroleum products. Thus these products need to be increased every year. Nowadays, the consumption of diesel was banned especially in developed countries such as New Delhi because it causes serious air pollution due to the emission of polluted gases such as carbon monoxide (CO), sulphur monoxide (SO) and other hazardous gases (Ramesh, *et al.*, 2002). Therefore, other alternatives are needed to solve this critical problem.

1.1.1 Source of Biodiesel

Biodiesel is one of the alternatives that have been found to substitute diesel fuel due to their similar properties. Biodiesel is biodegradable, almost sulphurless and a renewable fuel (Cardoso, *et al.*, 2008). Commonly, biodiesel is produced from vegetable sources such as soybeans, peanuts, rapeseeds as well as sunflowers (Ramesh, *et al.*, 2002). These vegetable oil sources can be divided into two categories which are edible and non-edible oils. As edible oils are much expensive than diesel fuel, non-edible oils are very suitable in biodiesel production. Example of edible oil are cardoon oil, Ethiopian mustard oil, gold-of-pleasure oil and tigernut oil while non-edible oil are bahapilu oil, castor oil, cottonseed oil, cuphea oil, *Jatropha curcas* oil, karanja seed oil, linseed oil, mahua oil, nagchampa oil, neem oil, rubber seed oil and tonka bean oil (Nag, 2008).

Agricultural wastes such as wood waste, palm oil kernel shell, empty fruit bunch, sago waste may also give bio-oil through pyrolysis. This type of biomass is abundant in Malaysia. Empty fruit bunch for example are produced more than 18 million tons according to its fresh weight (Khor, *et al.*, 2009).

1.1.2 Transesterification

Biodiesel is synthesized chemically through transesterification. Transesterification is a process of converting large, branched triglycerides which is oil source into smaller and straight chain molecule of alkyl esters by using alcohol in the presence of acid, base or enzyme catalyst (Lee, *et al.*, 2009). Alcohols such as methanol, ethanol, propanol, butanol and amyl alcohol are used in this process (Ramesh, *et al.*, 2002). Methanol is the most common alcohol used in transesterification because it is cheap, can reacts with triglycerides quickly, polar and shortest chain alcohol compared to other alcohol (Helwani, *et al.*, 2009).

1.1.3 Catalysts

In the production of biodiesel, there are some factors that affect the product yield. One of the factors is type of catalyst besides molar ratio of oil to alcohol, impurity content as well as reaction temperature and pressure (Lee, *et al.*, 2009). There are two types of catalyst which are acid catalyst and base catalyst. Acid-catalyzed transesterification is favoured if the oil source contains high free fatty acid (FFA). This FFA undergoes transesterification and converts to fatty acid methyl ester (FAME) or biodiesel. This type of transesterification yields high amount of alkyl ester. The disadvantage of this acid-catalyzed transesterification compared to base-catalyzed transesterification is its slow reaction (Lee, *et al.*, 2009). Therefore, the process takes long time to reach complete conversion and sometimes requires high temperature. For example, there is a study on acid-catalyzed transesterification using sulphuric acid (H_2SO_4) which takes 50 hours to reach complete conversion of soybean oil with methanol to oil molar ratio of 30:1 at 65^{o}C. Thus, in order to overcome this long process, the high amount of catalyst, large methanol to oil ratio within range 20-300:1 and high temperature of 150-250^{o}C are needed to speed up the reaction (Lee, *et al.*, 2009).

On the other hand, base catalysis is much faster and requires small methanol to oil molar ratio within range 5-15:1 as well as lower temperature between 60-75^{o}C only. More than 90% biodiesel is produced within 2 to 6 hours reaction time (Lee, *et al.*, 2009). Homogeneous base catalysts however are corrosive compared to heterogeneous base catalysts (Yan, Salley, *et al.*, 2008). Large amount of water are required to wash and remove the homogeneous catalysts after the reaction (Romero, *et al.*, 2011). Longer time is needed to reach complete separation phase. In addition, the catalysts can react with water and free fatty acids (FFA) in feedstock thus form soap which will weaken the catalytic activity (Helwani, *et al.*, 2009). Therefore, highly refined acid-free oil which contain FFA and water content less than 0.5% and 0.06% respectively as well as anhydrous alcohol should be used for these homogeneous catalysts (Yan, Salley, *et al.*, 2008). This may lead to high feedstock cost. The use of heterogeneous base catalysts such as alkaline metal hydroxides and alkaline earth metal oxide perhaps could overcome this problem. Among all heterogeneous base catalysts that have been used in transesterification, calcium oxide (CaO) catalysts have a high activity and tolerance to water and FFA about 2% and 3% respectively (Yan, Lu, *et al.*, 2008). Nanocrystalline CaO is much efficient catalyst (Bai, *et al.*, 2009).

1.2 Problem Statement

Agricultural wastes have abilities to be one of the alternative ways to produce biodiesel in order to substitute depleted diesel in the future. Palm oil mill effluent (POME) wastes obtained from Bau Palm Oil Mill (BAPOM), Sarawak, Malaysia were used in this project which by transesterification process, this waste was converted into useful biodiesel. However, the correct choice of catalysts may influence in the production of high yield of biodiesel. Previously, commercial production of biodiesel were used acid catalyst, however, the acidic properties in the biodiesel produced cause many problems and limitation such as container corrosion, sensitive to free fatty acid content in oil and catalysts active-site leaching. The use of homogeneous base catalysts may cause high production cost because they soluble in the solvent thus, many processes need to be done to purify the biodiesel. On the other hand, heterogeneous base catalysts are less problematic, much cheaper and easy to handle. So, the mix catalyst of homogeneous and heterogeneous base catalyst was introduced in this project in order to determine the effect of catalyst to the biodiesel production. Both catalysts have weaknesses when they were used alone and perhaps by mixing these two different catalysts might solve the problems.

1.3 Objectives

The objectives of this proposed project are:

1. To convert POME onto biodiesel through transesterification in the presence of solid base catalysts.
2. To determine the physical and chemical characteristics of the raw bio-oil.
3. To study the chemical and physical characteristics of the biodiesel.
4. To determine the effect of mix solid of CaO and sodium hydroxide (NaOH) to the biodiesel in the transesterification process.
5. To prepare raw bio-oil from other agricultural wastes such as wood waste and empty fruit bunch (EFB) via microwave pyrolysis and convert the bio-oil onto biodiesel.

CHAPTER 2

LITERATURE REVIEW

2.1 Biomass

Biological material that derived from living organisms such as plants, animals and microorganisms is known as biomass. Biomass can be utilized to produce energy and it is called bioenergy. For example, wood was used thousand years ago to provide heat for homes and cook foods.

Bioenergy is one of the renewable energy. It may reduce the impact of energy production and environmental friendly because it uses natural sources as the feedstock and will not harm the environment. This type of energy needs to compete with other renewable energy sources like wind, solar and wave power as well as fossil fuels in order to become one of the preferable energy sources (McKendry, 2002).

Three main products that are possibly produced from the conversion of biomass to bioenergy are heat generation, transportation fuel and chemical feedstock. Heat generation and transportation fuel are the products of energy-related. The conversion can be done by two major process technologies which are thermal-chemical and bio-chemical conversions. Thermal-chemical conversion consist four process options which are pyrolysis, combustion, gasification and liquefaction while digestion and fermentation are two process options for bio-chemical conversion. Mechanical extraction with esterification is another process technology available to convert biomass to energy. This process technology is preferably producing transportation fuel which is known as biodiesel (McKendry, 2002). Biodiesel is seems to be demanding fuel nowadays.

2.2 Biodiesel

The term biodiesel is referred as an alternative fuel in substituting standard diesel fuel. It is made up from various biological ingredients other than petroleum such as plants and animals especially agricultural waste. It can also be produced from new and used vegetable oils and animal fats (Bozbas, 2008). It is non-toxic, sulphurless and renewable as it comes from plants and animals (Cardoso, *et al.*, 2008). Biodiesel can be used in the diesel engines without any alteration and promisingly safe. It has similar physical properties to those of diesel fuel in terms of cetane number, energy content, viscosity and phase changes of fatty acid methyl ester (FAME) (Yee, *et al.*, 2008). However, it is much environmental friendly fuel. The usage of biodiesel instead of diesel may help the world in reducing the hazardous gases emission such as carbon monoxide (CO) and sulphur monoxide (SO).

Even though biodiesel can be used purely, usually it has been blended with standard diesel fuel for more effective function. Blend fuel are indicated by the abbreviation Bxx, where xx shows the percentage of biodiesel content in the blended fuel. For instance B20 where 20% of biodiesel is used in this mixed fuel (Foon, *et al.*, 2005). Biodiesel has been currently used in Malaysia and it is produced by Petronas Company as B5 Biodiesel with price RM 1.80 per litre which is similar to the Petronas diesel's price. The usage of neat biodiesel or 100% biodiesel may reduce the carbon dioxide emission by more than 75% over petroleum diesel (Bozbas, 2008). Thus, the environment can be protected.

Nowadays, people are trying to find out ways in order to produce biodiesel from various agricultural wastes especially palm trees which are much cheaper and profitable. Productions of biodiesel in Asian countries are using crude palm kernel oil and crude coconut oil while in USA and Europe they are using soybean and rapeseed as the feedstock (Yee, *et al.*, 2008) . This is due to the huge palm and coconut plantation in Asian countries.

2.3 Palm Oil Industry in Malaysia

Palm oil industry is one of the major contributors in Malaysia's economy. Both Malaysia and Indonesia are the largest exporter countries in oil palm product. The total areas of plantation are increasing every year. For example, in year 2000, plantation areas are increases to 3338 hectares from 320 hectares in 1970. Palm oil is extracted from palm fruit. One hectare of oil palm may produce approximately 10 to 35 tonnes of fresh fruit bunches (FFB) per year (Rupani, *et al.*, 2010).

2.3.1 Palm Oil Mill Effluent (POME)

The increasing in palm oil production throughout the year also contributes to increasing of the by-product of the milling process. Liquid waste named POME is generated from oil extraction process. Nearly 50% of the water contain in the POME (Okwute, *et al.*, 2007). For every tonne fresh fruit bunch, 0.5- 0.75 tonnes of POME will be discharged (Rupani, *et al.*, 2010). POME is physically thick and brownish semi-liquid and contains high solids, oil and grease, COD and BOD values (Rupani, *et al.*, 2010). It is one of the wastes generated which considered as the most dangerous waste for the environment if this type of waste is discharged untreated. This is because it contains highly oxygenated compound which may deplete the dissolved oxygen content in the water and cause the death of aquatic life because of the insufficient oxygen (Rupani, *et al.*, 2010). Therefore, before being discharged into the waterways, some treatment processes have been done on it in order to prevent its adverse affect to the environment.

POME also contains valuable nutrient compounds for example nitrogen. The presence of the nutrient compounds make POME to be used as fertilizer for agricultural crops when recycled to the soil. The effectiveness was proved when it grows up the young oil palm seedlings. Higher nitrogen can be found in the high total solid POME (Hashim, *et al.*, 1994).

2.4 Characteristics of POME

Characteristics of POME are due to the raw material quality as well as the production processes used in the palm oil mills. Raw POME has low pH value which is 4.7 (Rupani, *et al.*, 2010). POME is considered acidic waste as many types of fatty acids are reported found in the POME. Table 2.1 below shows the percentage of various types of fatty acid in the palm oil.

Fatty acids	**Percentages**
Palmitic acid	42.8
Oleic acid	40.5
Linoleic acid	10.1
Stearic acid	4.5
Myristic acid	1.0
Linolenic acid	0.2
Lauric acid	0.1

Table 2.1: Percentages of Fatty Acids in Palm Oil (Yee, *et al.*, 2008)

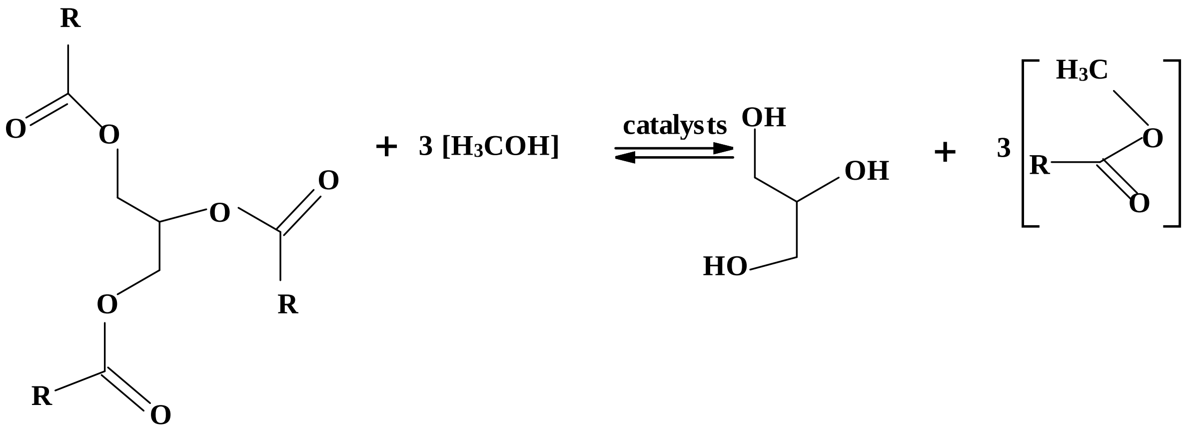
Table 2.2 shows the characteristics of raw POME. Raw as well as partially treated POME consists of high degradable organic matter content. POME is non-toxic waste as no chemicals are added during oil extraction process. However, it can causes aquatic pollution if discharged into the water bodies untreated (Rupani, *et al.*, 2010). Thus, the waste seems to be dangerous for the environment.

Parameters	Values (mgL^{-1})
Biochemical Oxygen Demand (BOD)	25 000
Chemical Oxygen Demand (COD)	50 000
Total Solids (T.S)	40 500
Total Suspended Solids (T.S.S)	18 000
Total Volatile Solids (T.V.S)	34 000
Oil and Grease (O & G)	4 000
Ammonia-Nitrate (NH_3-N)	35
Total Kjeldahl Nitrogen (TKN)	750

Table 2.2: Characteristics of Raw POME (Rupani, *et al.*, 2010)

2.5 Transesterification

Transesterification is a reaction of forming ester by mixing solvent and oil sources. Transesterification is an equilibrium or reversible reaction. The presence of catalysts in this process may alter and accelerate the adjustment of the equilibrium. Several types of catalysts can be used in transesterification such as homogeneous acid and base catalysts as well as heterogeneous acid and base catalysts. The transesterification reaction of triglycerides with methanol for the production of ester and glycerol is shown in Scheme 2.1.



Scheme 2.1: Transesterification Reaction

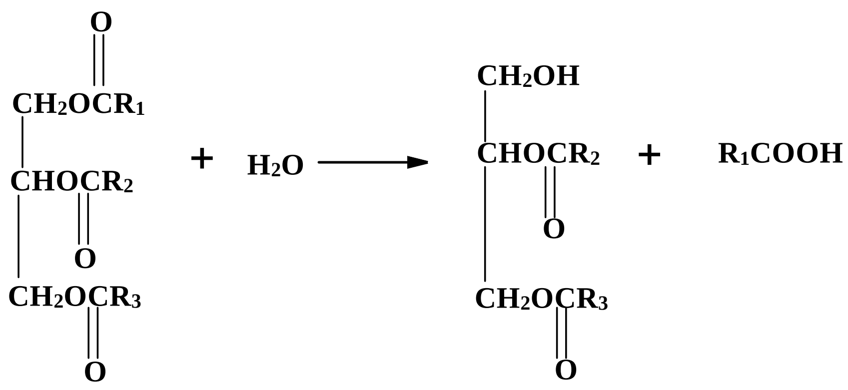
2.6 Homogeneous Acid and Base-Catalyzed Transesterification

Homogeneous base catalyst has been reported to be used in transesterification process. Sodium and potassium hydroxides (NaOH and KOH), carbonates, sodium and potassium alkoxides are commonly used as homogeneous base catalysts (Helwani, *et al.*, 2009). High quality biodiesel were obtained from the use of these catalysts as they showed high catalytic activity (Helwani, *et al.*, 2009). Glycerin or glycerol is also produced as by-product in transesterification. It is considered safe and can be used in pharmaceutical products like cream. It has to be removed from biodiesel. The failure of removing the glycerin may cause the formation of formaldehyde or acetaldehyde on combustion (Helwani, *et al.*, 2009). The presence of free fatty acid in the oil produced soap when they react with base catalyst. The soap generation causes lower yield of bio-oil and inhibited the separation of oil, glycerin and wash water. In addition, it also makes bonds with catalysts (Leung, *et al.*, 2010). Thus, more catalysts are required and it creates a problem in removing the catalysts from the product. Besides that, transesterification will take longer time thus increase the production cost. Scheme 2.2 shows the equation of saponification reaction of catalyst which is sodium hydroxide and the free fatty acid (FFA), forming soap and water.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

Scheme 2.2: Saponification Reaction of FFA

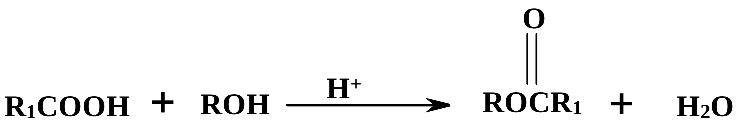
Water from the oil or FFA will cause conversion of triglycerides to diglycerides through hydrolysis reaction as well as the formation of more FFA and eventually cause retardation of transesterification process (Leung, *et al.*, 2010). The hydrolysis reaction of converting triglycerides into diglycerides is shown in Scheme 2.3.



Scheme 2.3: Hydrolysis Reaction

In homogeneous acid-catalyzed transesterification, the acid catalysts that are commonly used are sulphuric acid (H_2SO_4), hydrochloric acid (HCl) or sulphonic acid (Helwani, *et al.*, 2009). In order to afford good product yield, high alcohol to oil molar ratios need to be used (Helwani, *et al.*, 2009). The problem for this type of reaction is that ester yields do not proportionally increase with molar ratio. For example ester yield was improved from 87.8% to 98.4% when 6:1 ratio of methanol to oil changes to 30:1. Only 10.6% increment of ester yield can be obtained for higher molar ratio (Helwani, *et al.*, 2009). This may cause high production cost and consuming huge amount of methanol.

Homogeneous acid catalysts are different from base catalysts due to its reactivity on free fatty acid. Unlike base catalyst, acid catalyst is non reactive towards the free fatty acid in the oil thus will not form soap. In the presence of acid catalysts, the FFA will react with alcohol to form ester. This is because the reaction rate of this process is slower compared to catalysis by base (Leung, *et al.*, 2010). This clearly shows that acid catalysts can perform better than the base. The reaction of the FFA and alcohol in the presence of acid catalyst is shown in Scheme 2.4.



Scheme 2.4: Ester formation equation from reaction of FFA and alcohol

2.7 Heterogeneous Base and Acid Catalysts

Currently, researchers try to find out and explore new heterogeneous catalysts in order to substitute homogeneous catalysts which pose a few drawbacks such as wastewater generation and biodiesel loss due to the purification process. The major benefit of using heterogeneous catalysts is the easy separation of products formed without requirement of water for washing purposes. The removal of the catalysts from the products is just by filtration. Thus, the production cost can be reduced. Besides that, this type of catalyst is reusable as it does not form mixture with the products (Sharma, *et al.*, 2011).

There are two types of heterogeneous catalysts which are acid and base. The base catalysts have been reported as an effective catalyst in generating high yield of biodiesel compared to the acid catalysts. However, they are FFA-sensitive due to the basicity property. Thus, acid catalysts are much suitable to be used in producing biodiesel as they are not FFA-sensitive (Sharma, *et al.*, 2011). The long-term use of acid catalysts can cause corrosion to the fixed bed reactor due to the acidity property. The corrosive reactor is needed to be replaced to avoid the contamination of product. This may lead to increase the production cost. In addition acid and base catalysts are