

Heterogeneous Catalyst with Modified Rice Husk Catalyst Support from Natural Resources for Palm Fatty Acid Distillate (PFAD) Biodiesel Production

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# Heterogeneous Catalyst with Modified Rice Husk Catalyst Support from Natural Resources for Palm Fatty Acid Distillate (PFAD) Biodiesel Production

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> Faculty of Resource Science and Technology UNIVERSITI MALAYSIA SARAWAK

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# **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.

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### LIST OF ACHIEVEMENTS

- Patent: PI 2013004012. Ngaini, Z., Shahrom, F. D., & Jamil, N. (2013). Heterogeneous catalytic transesterification process for biodiesel production and other related matters.
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#### ABSTRACT

Biodiesel is an alternative energy source for diesel fuel. The utilisation of homogeneous catalyst such as sodium hydroxide in biodiesel production is commonly employed due to the high yield of biodiesel produced. Homogeneous catalyst however requires tedious additional step to separate from the reaction product. In this study, calcium oxide (CaO) was prepared from mussel's shells while rice husk ash was developed as a catalyst support to produce solid base catalysts (WSBC & GSBC) and solid acid catalysts (WSAC & GSAC), which prepared via chemical activation using NaOH and H<sub>2</sub>SO<sub>4</sub>, respectively. The catalysts were characterised using XRD, BET, SEM, and EDX analysis. The feedstock used in this study is a by-product from palm oil refining factory namely palm fatty acid distillate (PFAD). Due to the high FFA in PFAD, CaO was not suitable to be used in the direct transesterification reaction. PFAD underwent a two-step reaction, which is esterification using WSAC and GSAC followed by transesterification using WSBC and GSBC. Esterification of PFAD was performed in the ratio of MeOH:PFAD (1:1) in 2 h to afford 93 wt% yield of esterified PFAD. Transesterification of the esterified PFAD was performed in MeOH:esterified PFAD (1:1) in 30 min to produce PFAD biodiesel with 99.7% biodiesel conversion yield. The base supported catalysts have showed higher biodiesel conversion than CaO in the transesterification reaction. The biodiesel produced from PFAD possess similar properties with diesel fuel such as energy content (CV), thus exhibit greater potential to become one of the important energy sources in the future.

# PENGHASILAN PEMANGKIN HETEROGEN DARI SUMBER ALAM BAGI PENGELUARAN BIODIESEL DARI LEMAK KELAPA SAWIT (PFAD)

#### ABSTRAK

Biodiesel merupakan sumber tenaga alternatif bagi bahan api diesel. Penggunaan pemangkin homogen seperti natrium hidroksida dalam penghasilan biodiesel dipilih kerana dapat menghasilkan pengeluaran biodiesel yang tinggi. Pemangkin homogen bagaimanapun memerlukan langkah-langkah tambahan bagi memisahkan ia daripada campuran biodiesel. Kalsium oksida (CaO) yang dipeolehi dari cangkerang kepah dan abu sekam padi telah dikembangkan sebagai penyokong pemangkin untuk menghasilkan pemangkin alkali pepejal (WSBC & GSBC) dan pemangkin asid pepejal (WSAC & GSAC), yang disediakan melalui impregnasi menggunakan NaOH dan H<sub>2</sub>SO<sub>4</sub>. Pemangkin telah dicirikan menggunakan analisa XRD, BET, SEM, dan EDX. Bahan mentah untuk penghasilan biodiesel yang digunakan dalam kajian ini adalah daripada bahan buangan kilang penapisan minyak sawit iaitu asid lemak sawit sulingan (PFAD). Penggunaan CaO sebagai pemangkin tidak sesuai dalam transesterifikasi PFAD oleh sebab kandungan lemak asid bebas yang tinggi dalam PFAD. Seterusnya, PFAD menjalani dua langkah proses iaitu, esterifikasi menggunakan SAC diikuti oleh transesterifikasi menggunakan SBC. Pengesterifikasi PFAD dilakukan dalam nisbah MeOH: PFAD (1:1) dalam 2 jam untuk memberikan hasil sebanyak 93 wt% biodiesel. Transesterifikasi bagi esterif PFAD dilakukan dalam nisbah MeOH:esterified PFAD (1:1) dalam masa 30 min untuk menghasilkan PFAD biodiesel dengan 99.7% hasil penukaran biodiesel. Hal ini kerana pemangkin telah berjaya digunakan sebagai pemangkin heterogen untuk pengeluaran biodiesel daripada PFAD. Biodiesel yang dihasilkan daripada PFAD mempunyai ciri-ciri yang serupa dengan bahan api diesel seperti kandungan tenaga (CV), sekali gus berpotensi untuk menjadi salah satu sumber tenaga yang penting pada masa hadapan.

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# LIST OF ABBREVIATIONS

PFAD	Palm fatty acid distillate
FFA	Free fatty acid
RHA	Rice husk ash
WRHA	White rice husk ash
GRHA	Grey rice husk ash
ARHA	Activated rice husk ash
WARHA	White activated rice husk ash
GARHA	Grey activated rice husk ash
SAC	Solid acid catalyst
WSAC	White solid acid catalyst
GSAC	Grey solid acid catalyst
SBC	Solid base catalyst
WSBC	White solid base catalyst
GSBC	Grey solid base catalyst
FTIR	Fourier Transform Infrared
SEM	Scanning electron microscopy
BET	Brunauer-emmett-teller
XRD	X-ray diffraction
EDX	Energy dispersive X-ray
B100 PFAD	Pure PFAD biodiesel
B5 PFAD	Blended PFAD biodiesel
ASTM	America Standard Test Method

#### **CHAPTER 1**

#### **INTRODUCTION**

#### 1.1 Fossil fuel

Fossil fuel is the largest energy sources to produce energy. Dependency on fossil fuel as energy source has risen due to the increased of global urbanisation and standard living of society. The high reliance of fossil fuel has created concerns on its supply (EIA, 2014). The examples of depleting and highly consumed sources of fossil fuel are petroleum, natural gas and coal (EIA, 2014). In Malaysia, the average lifespans for oil and gas reserves are 25 and 39 years correspondingly (EPU, 2011). Due to the high dependency and shortage of oil and gas reserves in the future, biofuel was introduced as an alternative to lessen the dependency on petroleum fuel (Chin *et al.*, 2014).

Biofuel is a renewable source which able to overcome the scarcity of fossil fuel and air pollution (Chin *et al.*, 2014) as well as maintaining the carbon cycle in the environment (Puppan, 2002). Biofuel is a term that indicates liquid or gaseous fuel produced from biomass such as wood waste, potatoes and corn. The consumption of biofuel is favored due to its low level of sulfur, nitrogen and environmentally friendly (Puppan, 2002).

Biofuel can be divided into two categories, which are biodiesel and bioethanol. Bioethanol can be produced by fermentation of rich carbohydrate biomass such as corn, potato waste and wheat with the presence of enzyme and microorganism as catalysts. Bioethanol is used as an alternative to gasoline which operates in light vehicles (Puppan, 2002). Europe is the

largest country involve in producing and consuming ethanol from sugar-crops (corn, wheat, potato) plantation (EIA, 2006). Whereas, biodiesel is an ester based derived from vegetable oil, and used as an alternative to diesel fuel in heavy vehicles (Knothe *et al.*, 2005).

#### **1.2 Biodiesel**

Biodiesel is a mono-alkyl ester based oxygenated fuel derived from agricultural resources such as vegetable oil or waste cooking oil. It was introduced to replace petroleum-based diesel fuel due to its high degradability and renewability (Knothe *et al.*, 2005). In addition, biodiesel is safe to be used in conventional diesel engines with little or no modification done on the diesel engine (Demirbas, 2008). This is because biodiesel possesses similar properties with diesel engine in terms of cetane number, energy content and viscosity (Yee and Lee, 2008).

#### **1.2.1 Transesterifcation reaction**

Biodiesel is traditionally produced from transesterification reaction of vegetable oil (consist of triglycerides) with an alcohol in the presence of a catalyst (Clark *et al.*, 1984; Demirbas, 2008). The general reaction for transesterification of triglycerides is shown in Scheme 1.1 (Gerpen, 2005).



\*R : alkyl chain of different lengths fatty acids

Scheme 1.1: General reaction of Transesterification of triglycerides

#### 1.2.2 Catalyst

The selection of catalyst used is important for the efficiency in producing biodiesel (Demirbas, 2008). There are two main types of catalysts used in the transesterification reaction, which are homogeneous and heterogeneous catalyst. The application of homogeneous base catalysts such as sodium methoxide (NaOMe), sodium hydroxide (NaOH) (Raja *et al.*, 2011) and potassium hydroxide (KOH) (Marchetti *et al.*, 2007) are widely used in the production of biodiesel. These catalysts are cheaper and required less reaction time (Sharma *et al.*, 2010).

The production of biodiesel is commonly employing homogeneous catalyst. The reaction using homogeneous catalyst however require large amount of water usage and wastewater in the neutralisation step (Deutschmann *et al.*, 2009). The use of homogeneous base catalyst with feedstock containing high percentage of free fatty acids (FFAs) led to saponification reaction (Helwani *et al.*, 2009) and gave low yield of biodiesel. One of the alternatives to overcome these problems is by employing heterogenous catalyst (Lotero *et al.*, 2006; Sharma *et al.*, 2010).

Heterogeneous catalyst performs in a different phase from the reaction mixture. Due to the difference-working phase of the reaction mixture and catalyst, heterogeneous catalyst offered easy separation, reusability and cost reduction (Sharma *et al.*, 2010). Although heterogeneous catalyst allows easy separation, the formation of three phases (catalyst, oil, alcohol) contribute to diffusion limitation of the catalysts. This occurrence had lowered the effectiveness of the reaction (Mbaraka and Shanks, 2006). Thus, a catalyst support is developed as heterogeneous catalyst to overcome the problem (Zabeti *et al.*, 2009).

Silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) are the catalyst supports that commonly reported (Taufiq-Yap *et al.*, 2011; Arzamendi *et al.*, 2007). There are several studies reported on heterogeneous supported catalyst for biodiesel production such as NaOH/Al<sub>2</sub>O<sub>3</sub> (Taufiq-Yap *et al.*, 2011) and NaOH/SiO<sub>2</sub> (Arzamendi *et al.*, 2008). They are generally used as catalyst support due to their high surface area and porosity, which increase the active sites for impregnation with active species (Mbaraka and Shanks 2006) as shown in Figure 1.1.



Figure 1.1: Catalyst support with impregnated active species

Silica is usually obtained from natural soil such as volcanic rocks and clay (Drees *et* al., 1989; Mitra, 2014). Rice husk is another sources of silica from agricultural waste. About 90 - 97 % of silica is presence in the rice husk ash (Della *et al.*, 2002). The development of silica from rice husk has been reported as a support catalyst by impregnating with cobalt (Adam *et al.*, 2011) and ruthenium (Adam *et al.*, 2006; Artkla *et al.*, 2008). Less study reported on the utilisation of rice husk ash as heterogeneous catalyst for biodiesel production from waste feedstock.

#### 1.2.3 Feedstock

Besides catalyst, biodiesel feedstock is also one of the important factors in producing biodiesel. Vegetable oil such as soybean oil, rapeseed oil, sunflower oil, palm oil and coconut oil are commonly used as biodiesel feedstocks. Besides vegetable oil, animal fats such as beef tallow (Ma *et al.*, 1998) and chicken fat (Gürü *et al.*, 2010) are also used in producing biodiesel.

Whilst biodiesel is widely preferred as alternative fuel, the production cost of biodiesel has increased along with petroleum-based diesel fuel price (Ma & Hanna, 1999). This phenomenon was due to the increased of price in vegetable oil. Furthermore, the used of vegetable oil as biodiesel feedstock is competing with human daily dietary.

An alternative usage of agriculture waste such as palm fatty acid distillate (PFAD) is introduced to overcome the problems. Several studies had reported on the utilisation of PFAD as biodiesel feedstock (Chongkhong *et al.*, 2007; Chongkhong *et al.*, 2009). However, due to the high content of FFA in PFAD, homogeneous acid catalyst such as sulfuric acid ( $H_2SO_4$ ) is used to reduce saponification during transesterification process (Knothe *et al.*, 2005). The use of acid however could cause corrosion to the batch reactor wall and harmed aquatic life when released the acid wastewater into the river (Leung *et al.*, 2010).

#### **1.3 Problem statement**

Catalyst is very important in biodiesel production as it helps to initiate the reaction rate. The catalyst can be categorized as homogeneous and heterogeneous catalyst. The use of homogeneous catalyst however requires additional washing and purification step to remove the excess catalyst. In contrast, heterogeneous catalyst such as calcium oxide (CaO) is easier to handle by simple filtration. CaO can be prepared from waste such as cockle shells thru calcination. The employment of heterogeneous catalyst on the other hand, could cause diffusion limitation problem with the reactants. Silica was reported as a suitable catalyst support in chemical reaction. Therefore in this study, rice husk ash, an agricultural waste, that comprised major content (90%) of silica (Della *et al.*, 2002; Adam *et al.*, 2006) was proposed to be used for the preparation of heterogeneous catalyst.

Biodiesel feedstock is also important in the production of biodiesel. Traditionally vegetable oil was used as biodiesel feedstock. Vegetable oil, however, is being consumed in human daily dietary. With regards to food competition issues, non-edible feedstock such as wood waste and palm oil mill waste has gained attention due to their abundance availability. Utilising waste as feedstock for biodiesel production would be able to reduce the cycle of greenhouse gas emissions. Palm fatty acid distillate (PFAD) is a type of by-

product generated from refining process in palm oil industry. Therefore, this study was conducted using PFAD can be an alternative and potential feedstock of biodiesel.

#### **1.4 Research objectives**

The objectives of this project are:

- 1. to synthesize heterogeneous catalyst from mussel's shell and rice husk
- to investigate the developed catalysts for the production of biodiesel using PFAD as feedstock
- 3. to determine the physical and chemical characteristics of biodiesel produced
- 4. to study the efficiency of biodiesel produced to diesel engine.

#### **1.5** Scope of study

There were 2 types of catalysts; homogeneous and heterogeneous catalyst discussed throughout this study. Calcium oxide (CaO) was prepared from mussel shell in order to replace commercial CaO to be used as heterogeneous base catalyst. A catalyst support was also discussed in the thesis to be developed into heterogeneous catalysts particularly from rice husk. The porosity and surface characteristic of a catalyst support had affected the efficiency of the developed heterogeneous catalysts. Meanwhile, PFAD biodiesel was used as the feedstock in the biodiesel production. The content of acid value and FFAs in PFAD had affect the traditionally transesterification reaction, which caused PFAD to underwent esterification reaction first before transesterification reaction.

### **CHAPTER 2**

#### LITERATURE REVIEW

#### 2.1 Energy resources

New renewable energy sources are widely explored to replace the non-renewable energy sources such as petroleum and natural gas to meet world's energy demand. Worldwide consumption of energy sources in 2012 (Fig. 2.1) shows that petroleum has been the most demanded sources (36%), which surpassed natural gas, nuclear and renewable resources (EIA, 2014).



Figure 2.1: Worldwide energy sources consumption in 2012

Petroleum is categorised as fossil fuel sources (Hubbert, 1956; FAO, 2005). Fossil fuel sources was reported to continue providing nearly 80% supply of world energy until the year 2040 (EIA, 2013). Based on the current rate of production, the average lifespans for Malaysia's oil and gas reserves are 25 and 39 years correspondingly (EPU, 2011). The prolong dependency of oil and gas will cause depletion of Malaysia's petroleum reserves by 2100s should no new discoveries of reserved oil are made. In view of this, biofuel was introduced as an alternative resource to lessen the dependency on fossil fuel. Besides, renewable sources were predicted to increase by 12% in the year 2040 due to the strict implement of biofuel usage mandate (EIA, 2014).

#### **2.2 Biofuel**

Biofuel is a term that indicates liquid or gaseous fuel produced from biomass such as wood waste, potatoes and corn (Demirbas, 2009). The usage of biofuel is increasingly explored due to its renewable resources, which are biodegradable and sustainable energy resources (Puppan, 2002). Biofuel is environmentally friendly with low emission of sulfur and nitrogen (Demirbas, 2008).

The increasing demand of renewable energy has increased world's production of biofuel by 6.0-6.2% in developed countries (British Petroleum Country, 2014). This phenomenon shows the potential of biofuel that would overcome the shortage of petroleum fossil fuel in the near future. Biofuel can be divided into two categories, which are bioethanol and biodiesel.

#### 2.2.1 Bioethanol

Bioethanol is produced by fermentation process of biomass that are rich in carbohydrate such as corn, potato waste and wheat, in the presence of enzyme or microorganism as catalysts (Demirbas, 2008). Bioethanol can be used in light vehicles to reduce dependency on petroleum-based gasoline (Puppan, 2002). United States, Brazil and Europe are among the largest countries involve in producing and consuming bioethanol due to their huge plantation of corn, wheat and potato (Coyle, 2008; EIA, 2006).

#### 2.2.2 Biodiesel

Prior to the existence of biodiesel, vegetable oil had been used as an alternative fuel for diesel engine. Vegetable oil unfortunately has higher viscosity than diesel fuel, which requires modification on the diesel engine to maintain the engine's performance (Kerschbaum and Rinke, 2004). The unmodified diesel engine would cause formation of deposits in engine due to incomplete combustion and lubricating problems (Meher *et al.*, 2006; Demirbas, 2008). Many different methods had been introduced to decrease the viscosity of the vegetable oil such as dilution, microemulsification, pyrolysis and transesterification (Demirbas, 2008). Among all, transesterification is the most preferable and less expensive method of changing large and branched structure of oil molecule sized to a smaller sized molecule (Van Gerpen, 2005).

#### 2.3 Advantages and disadvantages of biodiesel

Biodiesel had attracted significant attention as an alternative fuel in replacing fossil fuel in diesel engine. This is because biodiesel has higher renewability, lower sulfur and aromatic content and higher cetane number than diesel fuel (Ma & Hanna, 1999). In addition, the use of biodiesel enhances lubrication in the engine and widely accepted by vehicle manufacturers. Biodiesel has also contributed to the economic industry by reducing country's reliance on crude oil imports and providing new labor and market opportunities for domestic crops (Clarke *et al.*, 2003; Demirbas, 2008; Palz *et al.*, 2002).

Despite the advantages, there are some drawbacks of using biodiesel. Biodiesel was reported to have higher viscosity and also higher in cloud and pour point than commercial petrodiesel (Demirbas, 2008). Therefore, it is not suitable to be used in critical cold weather. This is because biodiesel will crystallize quickly and clog inside the engine system during cold weather. Other drawback is the high price of feedstock from refined vegetable oil which contributes to the increase in the cost production of biodiesel (Demirbas, 2008).

Several studies reported on the use of biodiesel blending ratio with diesel fuel to overcome higher viscosity, cloud and pour point of biodiesel (Bozbas, 2008). Meanwhile, due to the high price of vegetable oil, utilisation of non-edible and waste material such as waste cooking oil and grease waste as biodiesel feedstock able to reduce the cost in the biodiesel production (Kulkarni and Dalai, 2006; Moser, 2011).

#### **2.4 Biodiesel production**

#### 2.4.1 Transesterification

They are several types of reactions in the production of biodiesel. Transesterification is one of the simplest reactions to produce biodiesel (Van Gerpen, 2005). Biodiesel is commonly synthesized by a simple transesterification of oil or esterification of fats with methanol in the presence of basic or acidic catalyst (Van Gerpen, 2005; Van Gerpen and Knothe, 2005). Transesterification reaction is usually performed using refined and high quality oil, which contains merely triglycerides of fatty acids with the presence of a base catalyst to produce FAMEs or biodiesel (Di Serio *et al.*, 2006).

Theoretically, 3 moles of methyl ester and 1 mole of glycerol are produced when 1 mole of triglyceride reacted with 3 moles of methanol in transesterification of vegetable oil. Commonly, base or acid catalyst is employed in transesterification reaction. Homogeneous base catalyst such as sodium and potassium hydroxide however is preferred as it initiates the process faster than homogeneous acid catalyst (Canakci and Van Gerpen, 1999).

Transesterification is a reversible reaction. Excess alcohol is commonly used in the reaction to maintain the process to move forward (Knothe *et al.*, 2005). There are two important factors in transesterification reaction to obtain high biodiesel yield, which are catalysts and feedstocks (Lee *et al.*, 2009).

#### **2.5 Catalyst**

The word 'catalysis' was introduced in year 1836 by Jacob Berzelius (Moulijn *et al.*, 1993). Catalytic reaction is a process whereby the reactant(s) will form a complex with the catalyst and opens an easy route for transformation into required product(s). Petrochemical industry had established the importance of catalyst in achieving high percentage production process with a lesser time (Deutschmann *et al.*, 2009; Sharma *et al.*, 2010). Catalyst is one of the important factors besides ratio of methanol, reaction temperature and type of feedstock used in biodiesel production (Lee *et al.*, 2009). Several catalysts have been employed in the production of biodiesel such as enzymes, acid and base catalysts (Chongkhong *et al.*, 2007; Marchetti *et al.*, 2007; Sharma *et al.*, 2010).

#### 2.5.1 Enzyme as catalyst

Enzyme is one of the catalysts used in the production of biodiesel (Deutschmann *et al.*, 2009). The common enzyme reported in the production of biodiesel is lipase. Lipase can be extracted from different bacteria sources such as *Bacillus subtilis* and *Pseudomonas flourescens*. The application of lipase from different sources has been reported to give biodiesel yield >90% at different optimum temperature for different type of biodiesel feedstock used (Table 2.1).

**Biodiesel** Bacteria source of **Optimum conditions** Maximum (Temperature & reaction time) source enzyme yield (%) Soybean oil Pseudomonas 20°C and 12 h 92 flourescens Sunflower oil *Candida antarctica* 50°C and 15 h 97 Jatropha oil Chromobacterium 40°C and 10 h 92 viscosum 90 Waste cooking Bacillus subtilis 40°C and 72 h oil

Table 2.1: Biodiesel production by enzymatic reaction of lipase extracted from different bacteria sources (Bajaj *et al.*, 2010).

For instance, the use of lipase from *Pseudomonas flourescens* requires to be sustained at 20°C to produce high yield of biodiesel (92%). However, the reaction is really timeconsuming (12 h). Enzyme is very sensitive to temperature and pH changes as it is easily denatured (Al-Zuhair *et al.*, 2003). Therefore, more energy is required to sustain the conditions of the requisite parameters needed.

#### 2.5.2 Acid and Base catalyst

#### 2.5.2.1 Homogenous catalyst

Other than enzymes, acid and base catalyst are commonly used in the production of biodiesel. These types of catalysts can be categorised as homogeneous and heterogeneous catalyst (Sharma *et al.*, 2010). Homogeneous catalyst is a common and preferred catalyst for the production of biodiesel. It can be divided into homogeneous base and acid catalyst (Sharma *et al.*, 2010).

Base catalyst such as hydroxides and methoxides of sodium and potassium are common homogeneous base catalysts used in the transesterification of biodiesel from vegetable oil (Sharma *et al.*, 2010). The methoxides catalysts are reported to perform better than hydroxides due to the readily available methoxides ions at the beginning of the reaction (Freedman *et al.*, 1984). Commonly the catalyst is mixed with alcohol prior to the addition of feedstock to produce higher yield of biodiesel (Guo, 2006).

The mechanism of base-catalyzed transesterification is shown in Scheme 2.1. The alkoxide ion (**RO**<sup>-</sup>) formed in Step 1 is readily reacted with the carbonyl of triglyceride, which resulted in the formation of tetrahedral intermediate (Step 2). The intermediate will rearrange to produce alkyl ester and diglyceride ion (Step 3). The diglyceride ion will react with the protonated base catalyst to produce diglyceride molecule (Step 4) and readily to be reacted with alcohol to form monoglyceride. Glycerol is produced when glyceride ion reacted with protonated base catalyst (Step 5) (Ma *et al.*, 1999; Di Serio *et al.*, 2006; Meher *et al.*, 2006). These continuous steps produce 3 alkyl ester (biodiesel) molecules and a glycerol at the end of base-catalyzed transesterifiaction reaction.



Scheme 2.1: Base-catalyzed mechanism of transesterification on triglycerides

Although homogeneous base catalyst showed better performance in producing biodiesel, the catalyst itself is also prone to react with free fatty acid (FFA) from the feedstock and formed saponification (Scheme 2.2). This occurrence has contributed to expensive separation and neutralisation process (Schuchardt *et al.*, 1998). Saponification, however,

does not occur in the presence of acid catalyst. FFA in the feedstock will undergo esterification reaction for the formation of ester and water (Scheme 2.3) (Van Gerpen and Knothe, 2005).

RCOOH + NaOH ---- RCOONa + H<sub>2</sub>O

Scheme 2.2: Saponification reaction of FFA

 $RCOOH + R'OH \xrightarrow{H^+} ROCR' + H_2O$ 

Scheme 2.3: General esterification reaction of FFA and alcohol

Other than homogeneous base catalyst, homogeneous acid catalyst such as sulfuric acid (Canakci and Van Gerpen, 1999) and hydrochloric acid (Fadhil *et al.*, 2012) are commonly used in acid-catalyzed transesterification process. The mechanism of acid-catalyzed transesterification is shown in Scheme 2.4 (Meher *et al.*, 2004). The carbonyl is protonated to form carbocation (Step 1), and readily reacted with an alcohol for the formation of tetrahedral intermediate (Step 2). The intermediate eliminates glycerol and proton to produce an alkyl ester (Meher *et al.*, 2004).



Scheme 2.4: Acid-catalyzed mechanism of transesterification on triglycerides

The used of acid catalyst in transesterfication of triglycerides however, requires longer reaction time, consumes higher amount of solvent, temperature and pressure compared to base catalyst (Boocock *et al.*, 1996; Schuchardt *et al.*, 1998; Sharma *et al.*, 2010). Sulfuric acid was reported as one of the strongest homogeneous acid catalyst used in producing biodiesel from unrefined feedstock (Haas and Foglia, 2005). Although homogeneous catalyst afforded higher yield of biodiesel using either base or acid catalyst, the difficulty in separation and purification of biodiesel from the catalyst is still persisted (Van Gerpen and Knothe, 2005).
#### 2.5.2.2 Heterogeneous catalyst

Heterogeneous catalyst is a catalyst that exists in solid form and does not dissolve in the mixture of reactants. It allows easy separation from the product mixture, increases the reusability of the catalyst and generates much cheaper biodiesel manufacturing cost (Lotero *et al.*, 2006; Sharma *et al.*, 2011).

Similar to homogeneous catalyst, base and acid catalyst are two types of heterogeneous catalyst used in the production of biodiesel. Metal oxides such as calcium oxide (CaO) (Boey *et al.*, 2011; Boey *et al.*, 2012) and magnesium oxide (MgO) (Leclercq *et al.*, 2001) are commercially available heterogeneous base catalysts. CaO is a common heterogeneous base catalyst used in transesterification of various feedstocks such as soybean oil (Venkat Reddy *et al.*, 2006), palm oil (Artkla *et al.*, 2008; Buasri *et al.*, 2013), tallow oil (Hu *et al.*, 2011) and waste cooking oil (Boey *et al.*, 2012). Commercial CaO is expensive and alternatively can be obtained from the environment such as limestone (Stanmore and Gilot, 2005), eggshells (Viriya-Empikul *et al.*, 2010) and shell aquatic life (Guo and Fang, 2011; Rashidi *et al.*, 2011; Kouzu and Hidaka, 2012). Mussel is one type of seashell that commonly found in Sarawak and can be used as an environmental friendly source of CaO (Boey *et al.*, 2012; Buasri *et al.*, 2013; Hu *et al.*, 2011). Other examples of base heterogeneous catalysts are potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), zinc oxide (ZnO) and mixed oxides such as CaO-ZnO (Ngamcharussrivichai *et al.*, 2008) and MgO-Al<sub>2</sub>O<sub>3</sub> (Fraile *et al.*, 2009).

Heterogeneous acid catalyst on the other hand, is able to perform as catalyst in the production of biodiesel even though with high content of FFA feedstock. This is because

heterogeneous acid catalyst is non-sensitivity towards FFA, which is similar to homogeneous acid catalyst. Amberlyst-15, mineral salts such as aluminum phosphate, ferric sulfate and ferric alginate (Boey *et al.*, 2012) are the examples of heterogeneous acid catalyst used in biodiesel production. Heterogeneous catalyst has an advantage compared to homogeneous catalyst as it offers simple catalyst separation step via filtration and no neutralization step required (Leung *et al.*, 2010; Taufiq-Yap *et al.*, 2011).

The production yield of biodiesel employing heterogeneous catalyst, either base or acid, is reported to be slightly lower than using homogeneous catalyst. This is due to the formation of three phases, which are catalyst, oil and alcohol in the reaction mixture as in Fig. 2.2. The occurrence of 3 different phases produces diffusion limitation due to the insolubility of solid and liquid, thus lead to low production yield of biodiesel (Taufiq-Yap *et al.*, 2011).



Figure 2.2: Diffusion limitation phenomena

Owing to this phenomenon, a catalyst support was reported by incorporating with heterogeneous or homogeneous chemical/catalyst and acting as a platform of two different active species to become a new heterogenised catalyst (Mbaraka and Shanks, 2006).

#### **2.5.3 Catalyst support**

A catalyst support or support material is a solid substance whereby an active species such as metal, nanoparticle and oxides of chemical is impregnated (Figure 1.2) (Mabena *et al.*, 2011). The shape of the catalyst support can exists as fibrous, granular or bulky unit material. Besides, having high thermal stability is one of the most important factors of a catalyst support. Silica, titanium, alumina and zirconia are some examples of catalyst support studied (Chakrabarty, 1990; Mabena *et al.*, 2011; Taufiq-Yap *et al.*, 2011).

Silica is reported as a very suitable catalyst supported material based on its inertness and physical strength (Van Heerbeek *et al.*, 2002) besides alumina. There are several methods in the preparation of heterogeneous catalyst using catalyst support such as impregnation, anchoring, grafting, deposition-precipitation and chemical vapor deposition (De Jong, 1999). To date, several studies reported on the supported heterogeneous catalyst for biodiesel production. For example NaOH/Al<sub>2</sub>O<sub>3</sub> (Taufiq-Yap *et al.*, 2011; Arzamendi *et al.*, 2007), NaOH/SiO<sub>2</sub> (Arzamendi *et al.*, 2008) and K<sub>2</sub>O/RH-MCM-41 (Artkla *et al.*, 2008). Taufiq-Yap *et al.*, (2011) reported on the deposition of NaOH onto alumina to produce NaOH/Al<sub>2</sub>O<sub>3</sub> and employed in transesterification of palm oil. The newly heterogeneous catalyst works efficiently as 99% conversion of biodiesel was achieved (Taufiq-Yap *et al.*, 2011).

## 2.5.4 Rice husk ash as catalyst support

Rice husk is an abundant agricultural waste particularly in Asia. More than 400,000 metric tonnes of rice husk are generated annually in Malaysia (Abu Bakar *et* al., 2010; Kadir and

Ariffin, 2013). About 20% of ash is produced from rice husk and 90 - 97% of silica can be obtained from the ashes of rice husk (Della *et al.*, 2002; Adam *et al.*, 2006).

The development of silica from rice husk as a catalyst support has been studied *via* impregnation with cobalt (Adam *et al.*, 2011), ruthenium (Adam *et al.*, 2006), aluminum, gallium, indium and iron (Ahmed and Adam, 2007). To date, several studies reported on the supported rice husk ash (RHA) as heterogeneous catalyst for biodiesel production such as RHA-Li (Chen *et al.*, 2013), RHA-CaO from eggshell (Chen *et al.*, 2015) and sulfuric acid onto RHA (Li *et al.*, 2014).

#### 2.6 Feedstock for biodiesel

Biodiesel feedstock is reported as one of the major factors which contributes to 80% of the total cost of biodiesel production (Demirbas, 2008). Biodiesel is composed of fatty acid methyl ester (FAME), which traditionally prepared from edible vegetable oil *via* transesterification process (Meher *et al.*, 2004). Formerly, vegetable oil such as soybean, rapeseed, sunflower, palm and coconut oil had been used to produce biodiesel (Knothe *et al.*, 2005). Soybean oil has been the most common source of biodiesel feedstock in United States, whereas rapeseed oil and palm oil are widely explored as the feedstock in Europe and tropical countries, respectively (Knothe, 2002).

The used of vegetable oil as biodiesel feedstock causes high production cost as well as triggers global food crisis due to food shortage and competition with daily food consumption. Massive deforestation causes high greenhouse gas emissions in the future climate change due to high plantation demand of food crops to fulfill the supply of vegetable oil (Fargione *et al.*, 2008). Non-edible feedstock has become an alternative to the biodiesel feedstock. Jatropha oil (Foidl *et* al., 1996), animal fat, yellow grease and agricultural waste are examples of non-edible feedstock to replace vegetable oil for biodiesel production (Demirbas, 2008).

Although animal fats is one of the alternatives to replace edible oil, the usage is limited due to the high content of saturated fatty acids which requires additional process to convert into biodiesel. Moreover, the supply is insufficient to cater the biodiesel demands (Ma *et al.*, 1999). Agricultural waste from industrial residues as biodiesel feedstock has become an important feedstock as it found in large quantity, cheaper and profitable alternative of non-edible feedstock than food crops (Antizar-Ladislao *et al.*, 2008).

# 2.6.1 Palm oil industry in Malaysia

Up to 2007, palm oil has been reported as the global leading vegetable oil production with >30% production, followed by other vegetable oil product such as soybean, rapeseed and sunflower oil (Fig. 2.3) (Rosillo-Calle *et al.*, 2009).



Figure 2.3: World's vegetable oil production in 2007

Malaysia is one of the largest producers and suppliers of palm oil in the world other than Indonesia. Palm oil plantation area in Malaysia has been increasing from 54,000 ha in 1960s to 4.3 million ha in 2008 (Fig. 2.4) (MPOB, 2008). Palm oil has been reported to dominate other vegetable oil because of its cheaper cost supply and able to sustain in longer period of time. In addition, smaller plantation area is required for palm oil plantation compared to other vegetable oils (Lam *et* al, 2009). Malaysia has explored the benefits of palm oil as a source of biodiesel in fulfilling demands search for alternative and renewable energy (Lam *et al.*, 2009).



Figure 2.4: Palm oil tree

## 2.6.1.1 Palm oil biodiesel

Biodiesel produced from palm oil has similar fuel properties to petroleum-based diesel and met the international standard such as EN14214 and ASTM D6751 (Lam *et al.*, 2009). Biodiesel from palm oil has the lowest total production cost compared to rapeseed and soybean oil from European countries and United States, respectively. Malaysia has established palm-based diesel as diesel substituent since 1996. Palm oil biodiesel namely B5 (blended of 5% palm biodiesel and 95% petroleum-based diesel) has been tested and launched commercially in heavy vehicles (Sumathi *et al.*, 2008). Palm oil has also generated a by-product from the refining process of palm cooking oil such as palm fatty acid distillate (PFAD) (Nang *et al.*, 2009).

## 2.6.1.2 Palm fatty acid distillate (PFAD)

Residues from the palm oil processes can be served as reliable renewable energy sources due to their easy accessibility and large continuity resources (Rupani *et al.*, 2010). Malaysia is the second largest crude palm oil (CPO) producer with 15.82 million tonnes production per annum (MPOB, 2007). PFAD is a low cost by-product generated from the physical refining of CPO to produce refined palm oil (Fig. 2.5) (Nang *et al.*, 2009). PFAD is commonly used in the soap-making industry. PFAD is also used as animal feed ingredient and other intermediate products for the oleo-chemistry industry such as candles (Rupilius *et al.*, 2006).



Figure 2.5: Palm fatty acid distillate (PFAD)

PFAD exists in semi-solid at room temperature and melts to brown liquid upon heating. PFAD has high (FFA) content with more than 70%, compared to refined palm oil. Palmitic and oleic acid are the main FFAs present in PFAD, ranging from of 43.0-49.1% and 34.7-37.2%, respectively. PFAD contain traces of triglycerides along with unsaponifiable matters as residual (Ping and Yusof, 2009).

# **2.6.1.3** Palm fatty acid distillate (PFAD) as biodiesel's feedstock

Several studies reported on the possible conversions of PFAD to biodiesel. For example, Chongkhong *et al.* (2007) have effectively convert PFAD into PFAD biodiesel *via* 2-step reaction which are esterification using sulfuric acid and followed by transesterification using sodium hydroxide as respective catalysts. The final PFAD biodiesel produced has met Thai biodiesel standard and ASTM D6751-02. The usage of sulfuric acid and sodium hydroxide as catalyst however had cause difficulty because lots of water required during separation step of catalyst from biodiesel.

Biodiesel from PFAD has also been prepared using ion-exchanged resin as catalyst during esterification process to afford 45.7% biodiesel (Pattamaprom *et al.*, u.d). The use of PFAD as an alternative to biodiesel feedstock can eliminate biodiesel production cost as well as reducing the competition of edible oil as biodiesel feedstock (Demirbas, 2008).

#### **CHAPTER 3**

#### **MATERIALS AND METHODS**

#### **3.1 Materials**

PFAD was obtained from Bau Palm Oil Mill (BAPOM), Sarawak and stored at room temperature. Mussel's shells were collected from nearby river mangrove area at Samarahan, Sarawak, cleaned and burned in furnace at 1000°C. Rice husk was obtained from an open field in Samarahan area, cleaned, and burned in furnace at 800°C. Hexane, methanol and sodium hydroxide pallets were purchased from Merck (Darmstadt, Germany). Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (96%) was obtained from Fisher Scientific. Petroleum ether was obtained from J. T. Baker (Philipsburg, USA). All reagents and solvents were used as received without any further purification throughout the study.

## **3.2 Instrumental analysis**

The crystalline structure of the samples were analysed using X-ray Diffractometer (X-RD) (Automated Rigaku Miniflex) equipped with a scintillation counter at Faculty of Science and Technology, Universiti Malaysia Terengganu. The diffraction patterns were recorded over goniometer (2 $\theta$ ) from 3 – 80°.

The surface morphology and internal diameter of the samples were examined using Scanning Electron Microscope (SEM) (JEOL JSM-6390 LA). The sample was dried to

eliminate absorption of moisture, placed on a stainless steel plate and coated with a layer of aurum to avoid charging of electron during scanning process.

The total surface area and pore volume of the samples were studied using Brunauer Emmet Teller (BET) (Quantachrome ASIQC0000-3) at Faculty of Engineering, UNIMAS. The nitrogen adsorption-desorption isotherms of the samples were measured at 77 K by a static method. Samples were degassed at  $350^{\circ}$ C and BET equation was applied to five adsorption data taken at relative pressures below 0.55 in order to calculate the specific surface areas. The total pore volume was estimated from the volume of N<sub>2</sub> adsorbed at about 0.10 relative pressure.

The elemental composition percentage of elements present in the samples were determined using Energy Dispersive X-ray (EDX) (JEOL JSM-6390LA) at Faculty of Resource Science and Technology, UNIMAS. Liquid nitrogen was used as a system cooler. The voltage was 20.0 kV and energy range of 0-20 keV. The mass percentage of each element present in the sample was recorded.

The functional groups in the samples were characterised using Fourier Transform Infrared Spectroscopy (FTIR) (Thermo Scientific Nicolet iS10) at Faculty of Resource Science and Technology, UNIMAS. The solid sample was mixed with potassium bromide (KBr) powder at ratio 1:100 (sample/KBr) and prepared as pallet for analysis. For liquid sample, a small amount of sample was dropped and smudged as thin film on zinc-selenide (Zn-Se) disc. The FTIR spectra were recorded within the range of 4000-400 cm<sup>-1</sup>.

GCMS analysis was performed using Gas Chromatography Mass Spectroscopy (GCMS) (Shimadzu GC-MS model QP2010 Plus). The instrument was equipped with a non-polar capillary column (30.0 m x 0.25 mm i.d x 0.25 µm of film thickness) by employing helium (He) as a gas carrier with pressure at 71.8 kPa. The column flow rate is at 0.94 mL/min and temperature was maintained at 10 C/min for 10 minutes. The initial and final temperature was maintained at 110 °C and 220 °C respectively (Yee and Lee, 2008). The sample was diluted with hexane as solvent to produced 100 ppm concentration.

Calorific value of the product was determined using Oxygen Bomb Calorimeter (Parr 6400) at Faculty of Engineering, UNIMAS. The sample was weighed approximately 1.0000 g and placed in a metal capsule and the capsule was placed in the jacket. Ignition thread was tied from the jacket and touched the sample in metal capsule. The jacket was then placed in the bucket of the calorimeter. The initial and jacket temperatures were maintained at 29 - 30 °C. The bomb was filled with oxygen to 30 atmospheres.

#### 3.3 Methodology

## 3.3.1 Preparation of calcium oxide (CaO) from mussel's shell

Mussel's shells (1000 g) were cleaned and dried in the oven for 24 h. The dried shells were calcined at 1000°C for 18 h in a furnace to obtain calcium oxide (CaO) (700 g) (Kouzu *et* al., 2008). The prepared CaO was cooled to room temperature and kept in the desiccator.

## 3.3.1.1 Direct-transesterification of PFAD using prepared CaO

Prepared CaO (1.0 g) as catalyst was added into methanol (60.0 g) in three-necked round bottom flask, heated and stirred for 1 h at 65°C. Preheated PFAD (20.0 g) was added into the continuous stirred mixture and heated under reflux for 24 h. The mixture was cool to room temperature, filtered and excess methanol was evaporated under reduced pressure to obtain 15.0 g of product. Direct-transesterification of PFAD was performed by employing different percentage (5%, 10%, 20%) of CaO.

## **3.3.2 Preparation of catalyst support from rice husk**

#### **3.3.2.1 Production of rice husk ash (RHA)**

Rice husk was collected from rice mill in Sungai Besar, Selangor area. Rice husk (1000 g) were cleaned and dried in the oven for 3 days. The dried rice husk was calcined in a closed furnace at 800°C for 16 h, cooled to room temperature to obtain white rice husk ash (WRHA) (180.0 g) and grey rice husk ash (GRHA) (50.0 g).

## 3.3.2.2 Preparation of activated rice husk ash (RHA) as catalyst support

WRHA (50.0 g) was soaked in NaOH solution (50 mL, 20%) and stirred for 2 h at room temperature. The mixture was filtered, rinsed with distilled water and dried for 24 h. Concentrated sulphuric acid (99% H<sub>2</sub>SO<sub>4</sub>) was added dropwise, stirred and washed with distilled water to pH 7 (Wahi and Senghie, 2011). The sample was dried in oven at 80 °C for 24 h to produce white activated rice husk ash (WARHA) (47.0 g). These steps were repeated using GRHA to produce grey activated rice husk ash (GARHA) (46.0 g).

#### **3.3.2.3** Preparation of solid base catalyst (SBC) from activated rice husk ash

WARHA (20.0 g) was stirred in NaOH solution (20 mL, 5M) for 24 h at room temperature. Excess NaOH solution was decanted and the solid was heated at 700°C for 10 min (Refaat, 2011). The sample was cooled to room temperature to yield white-solid base catalyst (WSBC) (19.2 g) and kept in desiccator. These steps were repeated using GARHA to yield grey-solid base catalyst (GSBC) (19.0 g).

#### 3.3.2.4 Preparation of solid acid catalyst (SAC) from activated rice husk ash

WARHA (20.0 g) was soaked in concentrated  $H_2SO_4$  (20 mL, 95%) and stirred for 30 min. Excess of acid was decanted and the solid was heated in a furnace for 12 h at 100°C (Kastner *et al.*, 2012). The sample was cooled and rinsed with distilled water to remove excess  $H_2SO_4$ . The sample was dried in the oven at 80 °C for 24 h, cooled to room temperature to produce white-solid acid catalyst (WSAC) (18.9 g) and kept in desiccator. These steps were repeated using GARHA to produce grey-solid acid catalyst (GSAC) (18.7 g).

#### **3.3.3 Application of SBC and SAC for PFAD biodiesel production**

Optimisation parameters in the reaction were observed for both esterification and transesterification reaction of PFAD. The parameters observed were catalyst loading, reaction time and the ratio of methanol to PFAD for both reactions.

#### 3.3.3.1 Direct transesterification of PFAD using SBC

WSBC (1.0 g) was added into methanol (160.0 g) in three-necked round bottom flask. The mixture was heated and stirred at 65°C for 1 h. Preheated PFAD (20.0 g) was added into the stirred mixture and continue heating under reflux for 1 h. The mixture was cooled to room temperature and filtered. The excess methanol was removed using rotary evaporator to give thick yellow oil (14.0 g).

#### 3.3.3.2 Esterification of PFAD using SAC

WSAC (1.0 g) was added into methanol (20.0 g) in three-necked round bottom flask. The mixture was heated and stirred at 65°C for 1 h. Preheated PFAD (20.0 g) was added into the stirred mixture and continued heating under reflux for 1 h. The mixture was cooled to room temperature and filtered. The excess methanol was removed using rotary evaporator to produce yellow oil (18.0 g).

#### 3.3.3.3 Transesterification of esterified PFAD using SBC

WSBC (0.50 g) was added into methanol (10.0 g) in three-necked round bottom flask. The mixture was heated and stirred at  $65^{\circ}$ C for 1 h. Esterified PFAD (10.0 g) was added and continued heating under reflux for 1 h. The mixture was cooled to room temperature and filtered. Two layers were formed as biodiesel (7.8 g) and glycerol (2.0 g).

## 3.3.4 Determination of acid value (mgKOH/g) and free fatty acid (FFA) (%)

In a conical flask, a weighted amount of biodiesel was dissolved in ethanol (5 mL). 1 mL of phenolphthalein was added into the flask. The FFA in the sample was titrated with potassium hydroxide solution (0.1 N) until pink colour started to appear (Lubrizol, 2006; Banani *et al.*, 2015). Acid value and FFA (%) of the biodiesel was calculated using Equation 1 and Equation 2 (Banani *et al.*, 2015).

Acid value (mgKOH/g) =  $\frac{N_{KOH} \times MW_{KOH} \times V_t}{W_s}$  .....Equation 1

where,  $N_{KOH} = Normality of KOH used$   $MW_{KOH} = Molecular weight of KOH; 56.11 g/mol$   $V_t = Volume of titrant used$  $W_s = Mass of sample, g$ 

 $FFA \% = \frac{AV_s}{2}$  Equation 2

where,  $AV_s$  = Acid value of biodiesel, mgKOH/g

# 3.3.5 Determination of esterified PFAD percentage (%) yield formula

Percentage yield, % =  $\begin{pmatrix} W_e \\ W_p \end{pmatrix}$  x 100%......Equation 3 Where: W<sub>e</sub> = weight of esterified PFAD, g W<sub>p</sub> = weight of PFAD used, g

#### 3.3.6 Determination of conversion percentage (%) of biodiesel from esterified PFAD

formula

Biodiesel  
conversion, % = 
$$\left(\frac{\text{Initial AV} - \text{Final AV}}{\text{Initial AV}}\right) \times 100\%$$
.....Equation 4

Where:

Initial AV = Acid value of PFAD, 182.36 mg KOH/g Final AV = Acid value of sample, mg KOH/g

# 3.3.7 Determination of glycerol production yield (%) formula

$$G = \left(\frac{W_g}{W_e}\right) x \ 100\% \dots Equation \ 5$$

Where:

G = weight percentage of glycerol, wt%

We= weight of esterified PFAD, g

W<sub>g</sub>= weight of glycerol, g

# 3.3.8 Calorific value and combustion capability test analysis

B100 and B5 PFAD biodiesel were tested for calorific energy value using Bomb Calorimeter. The PFAD biodiesel was applied in a combustion test of B100 PFAD biodiesel using alternative diesel engine at Politeknik Kuching, Sarawak. Note: B100 = 100% PFAD biodiesel, B5 = 5% PFAD biodiesel and 95% of petroleum diesel.

# **3.3.9 MS 2008:2008 and MS 123:2011 standard analysis**

The physical and chemical properties of B100 PFAD and B5 PFAD were tested by SIRIM Berhad, Shah Alam. B100 PFAD was analysed following MS 2008:2008 standard (Automotive Fuel-Palm Methyl Ester for Diesel Engine Requirements and Test Methods) while B5 PFAD was tested based on MS 123:2011 standard (Diesel Fuel Specification Part 1:Euro 2M). Note: B100 = 100% PFAD biodiesel, B5 = 5% PFAD biodiesel and 95% of petroleum diesel.

## **CHAPTER 4**

#### **RESULTS AND DISCUSSION**

#### 4.1 Preparation of heterogeneous catalyst from mussel shell

Calcination of 1000 g mussel at 1000 °C afforded 700 g of white powder CaO. During calcination, the calcium carbonate (CaCO<sub>3</sub>) in mussel shell was converted to CaO by the releasing of CO<sub>2</sub> (Buasri *et al.*, 2013).



Figure 4.1: (a) Mussel (b) CaO prepared by calcination

CaO obtained was characterised using XRD analysis for determination of crystallinity structure. The presence of narrow and high intense peak (Fig. 4.2) at  $2\theta = 29.60$  was defined as well-crystallized structure of molecules produced by the heat treatment process at 1000°C (Boey *et al.*, 2011; Hu *et al.*, 2011). Crystallize-type of molecules was reported as producing stable catalyst (Palermo *et al.*, 2000).

CaO was further characterised using FTIR spectroscopy as shown in Fig. 4.3. A broad and sharp bands at 1406.14 cm<sup>-1</sup> and 871.22 cm<sup>-1</sup> were attributed to the presence of CaO respectively (Guan *et al.*, 2013). In addition, a sharp absorbance band at 3641.51 cm<sup>-1</sup> was

corresponded to the presence of -OH group, which caused by the immediate reaction of CaO with H<sub>2</sub>O from moisture in the air (Margaretha *et al.*, 2012; Garcia *et al.*, 2008).



Figure 4.2: The XRD spectrum CaO from mussel shell



Figure 4.3: FTIR spectrum of CaO from mussel shell

The surface morphology of the prepared CaO was examined using SEM (Fig. 4.4). Irregular shaped particles were observed with the size in the range of 20-40  $\mu$ m. The mass percentage of calcium (Ca) (54.50%), oxygen (O) (36.73%) and carbon (C) (8.77%) were also analysed using EDX (Appendix A1) with high mass percentage of Ca and O.



Figure 4.4: SEM micrograph of prepared CaO from mussel's shells using (a) 2000x magnification (b) 5000x magnification

## 4.2 Attempted of direct-transesterification of PFAD using CaO from mussel

Having CaO prepared, direct-transesterification of PFAD was then performed adapting method by Van Gerpen (2005) with slight modification in the amount of catalyst. Different amount of CaO as catalyst (5 wt%, 10 wt% and 20 wt%) were used with a ratio of MeOH:PFAD (3:1). After 24 h reaction, CaO was removed by filtration to afford thick and viscous oily product in every percentage of catalyst used. In comparison to PFAD (Fig. 4.5a), FTIR spectra of direct transesterification of PFAD (Fig. 4.5b-d) showed the presence of two absorbance peaks at 1707.0 and 1744.1 cm<sup>-1</sup> attributed to carboxyl and ester group respectively, which indicated the incomplete formation of ester.



Figure 4.5: IR spectra of a) PFAD b) product by utilising 3:1 (MeOH:PFAD) with 5 wt% of CaO c) 10 wt% of CaO d) 20 wt% of CaO in 24 h reflux

No significant differences in the absorbance peaks of ester upon utilisation of 5 wt%, 10 wt% and 20 wt% of CaO (Fig. 4.5b-d). Ma and Hanna (1999) reported that excess of methanol would lead to the complete formation of ester. Reaction was then proceeded by increasing the ratio of MeOH:PFAD to 8:1 under reflux for 24 h.



Figure 4.6: IR spectra of product by utilising 8:1 (MeOH:PFAD) with a) 5 wt% of CaO b) 10 wt% of CaO c) 20 wt% of CaO

Semi solid product was formed at room temperature and characterised using FTIR (Fig. 4.6). Incomplete transesterification was still observed with the appearance of two absorbance peaks at 1743.1 cm<sup>-1</sup> and 1707.0 cm<sup>-1</sup>, attributed to carboxyl and ester group (Fig. 4.6a). The intensity of the ester group was not increased upon utilisation of 5 wt%, 10 wt% and 20 wt% of CaO (Fig. 4.6a-c).

An acid value (AV) of PFAD was determined via acid base titration (Section 3.3.4) to give 182.36 mgKOH/g and contain 91.18% of FFA (Appendix B1). The acid value and FFA% obtained in PFAD was too high, which exceeds the applicable value (3%) to undergo transesterification reaction (Meher *et al.*, 2006). The production of biodiesel from feedstock with high FFA content has been reported to undergo esterification reaction *via* acid catalyst prior to transesterification (Chongkhong *et al.*, 2007). Therefore direct-

transesterification of PFAD using CaO from mussel shell was not suitable in this reaction and pursued no further.

# 4.3 Preparation of silica-based heterogeneous catalyst from rice husk

Heterogeneous catalyst is favored in a reaction due to easy separation and able to be recycled. However, there is an occurrence of diffusion limitation of the catalyst into the reactants mixture due to the formation of three phases; oil, alcohol and catalyst (Mbaraka and Shanks, 2006; Taufiq-Yap *et al.*, 2011). Thus causing the reaction to slow down they are immiscible towards each other. Catalyst support has been reported to be one of the ways to overcome this circumstance (Taufiq-Yap *et al.*, 2011).

Silica and alumina have been earlier discussed (Chapter 2) and used as catalyst support in the production of biodiesel (Artkla *et al.*, 2008). Catalyst support is able to provide surface area and pores for the catalyst to attach and accelerates the reaction (Arzamendi *et al.*, 2008; Taufiq-Yap *et al.*, 2011). In this study, rice husk was chosen as a source of silica. Rice husk has been reported as having high content of ash (14-25%) with silica as high as 90-97% (Adam *et al.*, 2006; Della *et al.*, 2002). The rice husk collected was calcined at 800°C to form rice husk ash (RHA). 2 layers of ashes, white (WRHA) (180 g) and grey (GRHA) (50 g) were collected and further characterised.

#### 4.3.1 Crystallinity analysis via XRD

Both ashes (WRHA and GRHA) were characterised using XRD to determine silica crystallinity structure. Both WRHA and GRHA gave similar XRD pattern with the existence of a strong sharp peak at  $2\theta$ = 21.68, which indicates the presence of cristobalite (SiO<sub>2</sub>) in crystalline form (Fig. 4.7). High calcination temperature (>550°C) of rice husk had lead to the formation of cristobalite type of silica (Della *et al.*, 2002). Silica or silicon dioxide can exist as quartz, cristobalite and tridymite where cristobalite is the most stable structure for SiO<sub>2</sub> (Hosokawa *et al.*, u.d). Cristobalite silica has been reported to generate more effective and selective catalyst (Palermo *et al.*, 2000).



Figure 4.7: The XRD pattern of rice husk ash (RHA)

## 4.3.2 Morphological surface analysis via SEM

The surface morphology of the samples has been observed under SEM. The SEM micrograph of raw rice husk is shown in Figure 4.8(a). Smooth surface was observed on

the rice husk before underwent calcination. Layers of lignin and cellulose were observed at the cross section of rice husk (Fig. 4.8a). Porous surface (Fig. 4.8b-c) were formed after calcination of rice husk with pore in sizes in the range of 0.3-3.0 µm. Calcination at 800°C has removed the lignin and cellulose from the rice husk. Some agglomerated particles could also be seen on the surface of both ashes (WRHA and GRHA) indicated the existence of impurities, which can be removed further by chemical activation (Lehmann and Joseph, 2009).





Figure 4.8: SEM micrographs of (a) rice husk and cross section of rice husk (b) WRHA (c) GRHA

Both WRHA and GRHA was then activated by NaOH solution (20%). WARHA and GARHA micrograph showed the formation of more micro porous after underwent chemical activation with NaOH solution (Fig. 4.9). This was due to the activation by sodium that gave rise to more interlayer space and eventually increase the porosity (Lehmann and Joseph, 2009). During chemical activation, NaOH was responsible to

remove organic materials and develop micro porous structure (Wan Nik *et al.*, 2006). Further chemical activation by NaOH able to prevent pore clogging from impurities such as tars (Malik *et al.*, 2007). Chemical activation has successfully improved the development of pores in WARHA and GARHA.



Figure 4.9: SEM micrographs of (a) WARHA (c) GARHA

The surface morphology of solid base and acid catalyst (SBC and SAC) prepared from both WARHA and GARHA were also characterised using SEM (Fig. 4.10). There was almost no visible pore was observed in WSBC (Fig. 4.10a). Needle-shaped sodium (Na) has attached and occupied the pores and onto the surface during the impregnation process to produce WSBC, thus proven the success of impregnation process. On the other hand, fewer pores and agglomerated particles could be seen in WSAC (Figure 4.10b). This might be due to the impregnation of acid groups from H<sub>2</sub>SO<sub>4</sub> *via* sulfonation on the surface of porous WARHA (Pua *et al.*, 2011).

Similar to WSBC, needle-shaped of Na has attached and occupied the surface in GSBC (Figure 4.10c). As for GSAC (Figure 4.10d), sulfonation of  $H_2SO_4$  has occupied the pore structure of GSAC to be occupied (Pua *et al.*, 2011), which was similar to SEM micrograph of WSAC.



Figure 4.10: SEM micrographs of (a) WSBC (b) WSAC (c) GSBC (d) GSAC

## 4.3.3 Surface area and pore volume analysis via BET

Apart from SEM, BET analysis was also performed onto the samples of white and grey ashes and the catalysts series to determine the total pore volume and surface area. All the BET results are shown in Appendix C and tabulated in Table 4.1. The total surface area of WRHA was 1.914 m<sup>2</sup>/g whereas the total pore volume was  $5.161 \times 10^{-4}$  m<sup>3</sup>/. The total surface area and pore volume for GRHA were 73.182 m<sup>2</sup>/g and 2.831 x 10<sup>-2</sup> m<sup>2</sup>/g respectively. Small surface area and pore volume could minimise the following impregnation process. The surface area and the pore size of the catalyst support were then maximized *via* chemical activation process to afford WARHA and GARHA (Molina-Sabio and Rodriguez-Reinoso, 2004; Lehmann and Joseph, 2009).

Sample	BET Surface Area (m <sup>2</sup> /g)	Pore Volume (m <sup>3</sup> /g)
WRHA	1.914	5.161 x 10 <sup>-4</sup>
WARHA	18.947	8.109 x 10 <sup>-3</sup>
WSBC	14.493	4.985 x 10 <sup>-3</sup>
WSAC	7.362	2.726 x 10 <sup>-3</sup>
GRHA	73.182	2.831 x 10 <sup>-2</sup>
GARHA	122.887	4.638 x 10 <sup>-2</sup>
GSBC	0.000	-5.346 x 10 <sup>-5</sup>
GSAC	70.946	2.829 x 10 <sup>-2</sup>

Table 4.1: BET total surface area and pore volume of all samples developed from WRHA and GRHA.

The total surface area detected for WARHA and GARHA were 18.947 m<sup>2</sup>/g and 122.887 m<sup>2</sup>/g respectively, which were higher than surface area of WRHA and GRHA respectively (Table 4.1). The increasing surface area and pore volume of a support material is very crucial in order to provide maximised attachment of active species onto the catalyst support during impregnation step (Taufiq-Yap *et al.*, 2011).

BET analysis was also performed onto WSBC and GSBC after impregnation with NaOH. The total surface area and pore volume detected for WSBC was 14.493 m<sup>2</sup>/g and  $4.985 \times 10^3$  respectively, which was lower than WARHA (Table 4.1). Similarly, the total surface area for GSBC was also decreased from GARHA. The decreasing of surface area and pore volume of both WSBC and GSBC indicated that sodium groups were successfully impregnated onto WARHA and GARHA (Taufiq-Yap *et al* 2011), which was shown by the presence of needle-shaped particles in SEM (Fig. 4.10 a & Fig. 4.10c). The

decreased on the surface area after impregnation process has also been reported in other similar studies (Arzamendi *et al.*, 2008; Taufiq-Yap *et al.*, 2011).

The total surface area and pore volume of WSAC and GSAC were also lower than WARHA and GARHA respectively after impregnation with H<sub>2</sub>SO<sub>4</sub>. The value for total surface area obtained for both WSAC and GSAC were 7.362 m<sup>2</sup>/g and 70.946 m<sup>2</sup>/g respectively (Table 4.1). The decreasing of surface area and pore volume of solid acid catalysts (WSAC and GSAC) indicates that  $-SO_3H$  groups were successfully impregnated onto WARHA and GARHA. Impregnation *via* sulfonation has been reported to decrease the surface area and pore volume because all the porous spaces were occupied by the  $-SO_3H$  groups (Liu *et al.*, 2010; Pua *et al.*, 2011).

#### 4.3.4 Elemental analysis via EDX

The types of element presence in samples (WRHA, WARHA, WSBC and WSAC) were characterised using EDX. The mass percentage of the following elements; silica (43.56%), oxygen (34.87%) and carbon (21.56%) were detected in WRHA as shown in Table 4.2.

	Mass percentage of element (%)					
Sample	Silica	Carbon	Oxygen	Sodium	Sulfur	
	(Si)	(C)	(O)	(Na)	<b>(S)</b>	
White Rice husk ash (WRHA)	43.56	21.56	34.87	-	-	
White Activated rice husk ash (WARHA)	36.48	28.41	35.11	-	-	
WSBC	33.22	29.98	36.39	0.40	-	
WSAC	41.34	19.20	36.21	-	3.25	
49						

Table 4.2: Elemental composition by EDX analysis

The mass percentage of elements in WARHA was varied after chemical activation process. A slight increase of oxygen (35.11%) was possibly due to the moisture absorbed from the environment (Freedman *et al.*, 1984). The mass percentage of silica (36.48%) and carbon (28.41%) was detected in ARHA (Table 4.2) with no traces of sodium.

In contrast, WSBC contain slightly higher mass percentage of carbon (29.98%) and oxygen (36.39%) but lower mass percentage of silica (33.22%). The increased of oxygen mass percentage could be due to NaOH which the hygroscopic properties of NaOH, which enable to absorb moisture from surrounding (Knolle *et al.*, 2003). The successful impregnation of NaOH onto WARHA indicates by the sodium mass percentage (0.40%) detected in WSBC. The impregnation of NaOH is shown by SEM image in Fig. 4.10a. Carbon (19.20%), oxygen (36.21%) and silica (41.34%) were also detected in WSAC (Table 4.2). Sulfur (3.25%) was detected in WSAC due to the presence of -SO<sub>3</sub>H after successfully impregnation of sulfur from –SO<sub>3</sub>H groups onto WARHA.

# 4.3.5 Functional group characterisation *via* FTIR

The functional group presence in white and grey RHA series were characterised using FTIR (Fig. 4.11). The absorbance peaks at 1100-950 cm<sup>-1</sup> in all samples attributed to the presence of SiO<sub>2</sub> (Bange *et al.*, 2008; Liou and Wu, 2010). The intensity of SiO<sub>2</sub> absorbance peak however decreased slightly and shifted in solid base and acid catalyst compared to the activated ash for both white and grey ashes. This was due to the impregnation of NaOH and -SO<sub>3</sub>H onto activated ash, which caused shifting on stretching vibration of SiO<sub>2</sub> (Sohn *et al.*, 1997).

The presence of absorbance peak at  $3403.9 \text{ cm}^{-1}$  in WSAC was attributed to -OH group due to the hygroscopic properties of H<sub>2</sub>SO<sub>4</sub> (Adam and Thiam-Seng, 2013). Absorbance peaks at 1438 and 1425 cm<sup>-1</sup> were observed in both WSBC and GSBC, respectively. These peaks were attributed to sodium crystallization (Contreras *et al.*, 2006). The SiO<sub>2</sub> peaks were observed and retained in all samples after underwent several chemical modifications.



Figure 4.11: FTIR spectra of samples

#### 4.4 Application of solid base and acid catalyst for biodiesel production

## 4.4.1 Attempted of direct-transesterification of PFAD using solid base catalyst (SBC)

Direct-transterification of PFAD was initiated by adapting method reported by Chongkhong *et al.* (2007) with slight modification on the amount of WSBC used. The reaction was performed with MEOH:PFAD ratio of 8:1 in the presence of 5 wt% WSBC under reflux. After 1 h reaction, WSBC was removed by filtration to afford thick and high viscous oily product. FTIR spectrum (Fig. 4.12a) only showed peak at 1669 cm<sup>-1</sup> attributed to carbonyl from PFAD. No formation of ester group was observed. The transesterification of PFAD was then prolonged to 24 h and characterised using FTIR. The FTIR spectrum (Fig. 4.12b) showed a mixture of carboxyl and ester group at 1707 cm<sup>-1</sup> and 1741 cm<sup>-1</sup>, respectively.



Figure 4.12: IR spectra of product by utilising MeOH:PFAD ratio 8:1 with a) 5 wt% of WSBC in 1 h b) 5 wt% of WSBC in 24 h c) 10 wt% of WSBC in 24 h d) 20 wt% of SBC in 24 h e) 20 wt% of GSBC in 24 h

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The insufficient amount of catalyst was believed as the main reason for the incomplete ester formation (Taufiq-Yap *et al.*, 2011). Transesterification of PFAD was then performed by increasing the amount of catalyst up to 10 and 20 wt% with constant MeOH:PFAD ratio of 8:1 and heated under reflux for 24 h. The FTIR spectra showed the presence of both carboxylic and ester groups using both 10 and 20 wt% WSBC (Fig. 4.12c-d). Similar FTIR analysis was observed by utilising GSBC (20 wt%) as catalyst in direct transesterification of PFAD (Fig. 4.12e). The high content of free fatty acid (FFA) of PFAD was believed to hinder the base-catalyzed transesterification process (Chongkhong *et al.*, 2007). PFAD was then esterified using acid catalyst followed by transesterification reaction (Ramadhas *et al.*, 2005; Ping and Yusof, 2009).

## 4.4.2 Esterification of PFAD using solid acid catalyst (SAC)

## 4.4.2.1 Effect and optimization on catalyst loading and reaction time

Esterification reaction of PFAD was performed using WSAC by adapting method by Chongkhong *et al* (2007) with slight modification. MeOH:PFAD ratio (8:1) was used in the presence of 1 wt% WSAC in different reaction times. High ratio value was initially used according (Chongkhong *et al.*, 2007). High assist ant Yellow viscous oily product was obtained and analysed using FTIR (Fig 4.13). There has been an increasing in the intensity of ester group at 1741 cm<sup>-1</sup> at different reaction times with traces of carboxylic group at 1710 cm<sup>-1</sup>.



Figure 4.13: IR spectra of product by utilising MeOH:PFAD ratio 8:1 with 1 wt% WSAC in reaction time a) 1 h b) 2 h c) 3 h d) 24 h

The increased amount of catalyst utilised in biodiesel production was capable to upsurge the biodiesel conversion (Taufiq-Yap *et al.*, 2011). The amount of WSAC was therefore increased up to 5 wt% and observed hourly (Fig. 4.14). Complete conversion of ester was observed using 5 wt% WSAC at 2 h reaction time (Fig. 4.14b). The ester formation also remains stable during 3 h reaction time, which can be observed by the presence of only ester group peak at 1741 cm<sup>-1</sup> (Fig. 4.14c).



Figure 4.14: IR spectra of product by utilising ratio MeOH:PFAD (8:1) with 5 wt% of WSAC in a) 1 h b) 2 h c) 3 h

## 4.4.2.2 Effect and optimisation on ratio of MeOH:PFAD

After successful esterification using MeOH:PFAD (8:1), the optimisation of MeOH:PFAD was performed using different ratios (5:1, 3:1, 1:1, 0.5:1) with constant WSAC amount (5 wt%) in 2 h. Yellow oily product was obtained and analysed using FTIR analysis (Fig. 4.15). Complete conversion of carboxyl group to ester was achieved using MeOH:PFAD (1:1) (Fig. 4.15a-c) in 91.6% yield (Appendix D1). Traces of carboxyl group was observed in MeOH:PFAD with ratio 0.5:1 (Fig. 4.15d).


Figure 4.15: IR spectra of product by utilising 5 wt% of SAC in 2 h with ratio MeOH:PFAD a) 5:1 b) 3:1 c) 1:1 d) 0.5:1

Esterification of PFAD was also performed using GSAC with the same optimum ratio and reaction conditions to afford yellow oily product with slight increase of yield 93% (Appendix D2).

The esterified PFAD was furthered characterised using GCMS to confirm the composition of the esterified PFAD (Table 4.3). No significance carboxyl group was detected in esterified PFAD, compared to PFAD GCMS (Table 4.4) spectrum (Appendix E). Palmitic acid, for instance, was converted completely into methyl palmitate, which indicates complete conversion of carboxyl group into ester.

Peak	Retention	Height	Molecular	Molecular	Compound
	time	%	formula	weight	name
1	19.576	4.51	$C_{15}H_{30}O_2$	242	Methyl
					tetradecanoate
3	21.940	34.67	$C_{17}H_{34}O_2$	270	Methyl palmitate
9	24.787	39.39	$C_{19}H_{36}O_2$	296	Methyl oleate
10	25.189	18.82	$C_{19}H_{38}O_2$	298	Methyl stearate

Table 4.3: The composition of the esterified PFAD

Table 4.4: The composition of PFAD

Peak	Retention	Height	Molecular	Molecular	Compound
	time	%	formula	weight	name
1	19.190	2.82	$C_{15}H_{28}O_2$	240	Dodecyl acrylate
2	21.910	4.07	$C_{17}H_{34}O_2$	270	14- Methyl pentadecanoate
3	22.545	73.99	$C_{16}H_{32}O_2$	256	Palmitic acid
6	25.544	13.25	$C_{18}H_{34}O_2$	282	Oleic acid

The acid value of esterified PFAD was also calculated (Section 3.3.4) to give 6 mgKOH/g (Appendix B2). Esterified PFAD consisted 3% of FFA (Section 3.3.4), which was in the range of 3% and suitable to undergo base catalysed-transesterification reaction (Meher *et al.*, 2006).

# 4.4.3 Transesterification of esterified PFAD using solid base catalyst (SBC)

Transesterification of the esterified PFAD was performed following method reported by Boey *et al.*, (2012) with slight modification. MeOH:esterified PFAD (1:1) was reacted in the presence of 5 wt% WSBC in 1 h. After filtration of the catalyst, thick and viscous product was obtained. FTIR spectrum showed sharp peak at 1741 cm<sup>-1</sup> indicating ester group was observed in the product (Appendix F1). Addition of distilled water onto the product produced cloudy solution (Fig. 4.16a). This phenomenon could be due to the excess NaOH reacted with water molecules and acted as hygroscopic material thus dried up the product (Knolle *et al.*, 2003). This has caused difficulty in glycerol separation from the product. Therefore, the amount of WSBC was reduced to prevent NaOH leached out from the catalyst.

The transesterification reaction was then performed in the presence of 1 wt% WSBC with constant MeOH:esterified PFAD ratio (1:1) in 1 h. After filtration of the catalyst, two layers were produced as biodiesel and glycerol respectively (Fig. 4.16b). FTIR spectrum showed sharp absorbance peak at 1742 cm<sup>-1</sup> attributed to ester group (Appendix F2). The formation of glycerol has confirmed the success of transesterification using WSBC as solid base catalyst.





Figure 4.16: Physical appearance of biodiesel produced upon utilising a) 5 wt% WSBC b) 1 wt% WSBC

## 4.4.4 Comparisons on WSBC, GSBC, NaOH and CaO as base catalyst

Having biodiesel and glycerol produced from transesterification of esterified PFAD, comparisons using different base catalysts (WSBC, GSBC, NaOH and CaO from mussel) were performed using the same ratio parameters (MeOH:esterified PFAD, 1:1).

# 4.4.4.1 Conversion percentage (%) of biodiesel from esterified PFAD

The percentage yield (%) of biodiesel from esterified PFAD was determined based on percentage difference in acid (Banani *et al.*, 2015) (Appendix G1). The reaction was performed using the same parameters (MeOH:esterified PFAD 1:1, 1 wt% catalyst) in different reaction time. The percentage conversion of esterified PFAD to biodiesel using WSBC, GSBC and CaO is shown in Figure 4.17.



Figure 4.17: Biodiesel conversion yield (transesterification using WSBC, GSBC, CaO)

Figure 4.17 showed the biodiesel produced had reached the highest yield using WSBC and GSBC with 99.7% conversion compared to CaO (96.3%) at 30 min reaction time. WSBC and GSBC showed the most effective catalyst usage in terms of the highest biodiesel conversion (>97%) obtained.

NaOH (3M) was also employed as catalyst in transesterification of esterified PFAD using the same parameters MeOH:esterified PFAD (1:1) and 1 wt% NaOH. Thick and viscous oil was produced starting 30 min reaction time, which was similar to the previous phenomenon in Fig. 4.16a. Emulsion was formed upon purification with H<sub>2</sub>O and caused difficulty in glycerol separation from desired biodiesel. This phenomenon proved the incompatibility of NaOH as catalyst during transesterification of the esterified PFAD, which requires additional neutralisation and washing step.

#### 4.4.4.2 Glycerol production yield (%) from transesterification of esterified PFAD

The optimization yield of biodiesel was also performed by the observation on glycerol formation yield (%) during transesterification of esterified PFAD. The reaction was performed using the same parameters (MeOH:esterified PFAD, 1:1; 1 wt% catalyst) in different reaction time. The amount of glycerol produced was calculated (Section 3.3.7) and the wt% of glycerol produced for each reaction time was determined (Appendix H1).

It was observed that the formation of glycerol was increased with the reaction time and started to be constant at 30 - 90 min with 21.0 wt% and 19.0 wt% of glycerol produced, using WSBC and GSBC as catalyst, respectively (Fig. 4.18). In other words, the optimised

reaction time for the transesterification of esterified PFAD was 30 min with 21.0 wt% of glycerol produced.



Figure 4.18: Weight percentage of glycerol in different reaction time

Apart from WSBC, GSBC and NaOH, CaO from mussel prepared earlier, was also applied as base catalyst in the transesterification reaction of esterified PFAD. 1 wt% and 5 wt% of CaO were employed with the same parameter MeOH:esterified PFAD (1:1) used in different reaction time. There was a slow increased in the glycerol produced as 1 wt% of CaO used as catalyst. The yield of glycerol was increased when 5 wt% of CaO was employed. The yield of glycerol, was still gradually increased in 24 h of reaction time (Fig. 4.19). This scenario indicated that more reaction time required for the completion of transesterification. Therefore, it can be concluded that WSBC and GSBC were more efficient as base catalyst compared to CaO and NaOH.



Figure 4.19: Weight percentage of glycerol in different amount of CaO used and reaction time

From both approaches (Section 4.4.4.1 and 4.4.4.2), the observation method on the glycerol formation from the transesterification reaction gave simpler techniques than the method on the conversion (%) of biodiesel from esterified PFAD. However, determination on the conversion (%) of biodiesel from esterified PFAD gave more accurate findings, which provides the value of 99.7% of the esterified PFAD had been successfully converted into PFAD biodiesel by using WSBC and GSBC as base catalysts.

### 4.5 Physical and chemical characterisation of optimised PFAD biodiesel

## 4.5.1 GCMS analysis

The biodiesel produced from two-step reaction of PFAD was characterised using GCMS. The composition of the biodiesel is tabulated in Table 4.5. The chromatogram is shown in Appendix E3. Methyl palmitate (34.43%) and methyl oleate (57.86%) gave the highest ester percentage present in PFAD biodiesel. Methyl palmitate and oleate were the major ester compounds presence due to the high palmitic and oleic acid found in palm tree (Yee and Lee, 2008) and as shown in PFAD GC chromatogram (Appendix E1). No significance carboxyl group was detected in PFAD biodiesel as shown in Table 4.5.

Peak	Retention	Area %	Molecular	Molecular	Compound
	time		formula	weight	name
1	21.940	34.43	$C_{17}H_{34}O_2$	270	Methyl
					palmitate
2	24.704	57.86	$C_{19}H_{36}O_2$	296	Methyl oleate
2	25.116	0.11		200	
3	25.116	3.11	$C_{19}H_{38}O_2$	298	Methyl stearate

Table 4.5: The composition of optimised biodiesel

## 4.5.2 Acid value and pH analysis for biodiesel

Acid value is one of the properties that show the quality of biodiesel (Leung *et al.*, 2010). The initial acid value calculated (Section 3.3.4) for PFAD was 182.36 mgKOH/g (Table 4.6i) (Appendix B1). The acidity of PFAD decreased after underwent both esterification and transesterification reaction, which gave B100 PFAD biodiesel an acid value of 0.49 mgKOH/g (Appendix B3). According to the European biodiesel standard (EN 14 104), the acid value to be able run in diesel engine should not exceed 0.50 mgKOH/g (Knothe *et al.*, 2005).

Entry	Sample	Acid value, AV	Free fatty	pH value
		(mg KOH/g)	acid, FFA %	
i	PFAD	182.36	91.18	4
	Esterified	6.01	2.01	6
11	PFAD	0.01	5.01	
iii	B100 PFAD	0.49	0.25	8

Table 4.6: The acid value, free fatty acid content and pH for PFAD, Esterified PFAD and B100 PFAD

The pH value of PFAD, esterified PFAD and B100 PFAD was analysed using pH meter. pH for PFAD was found at 4-5, whereas for esterified PFAD and B100 PFAD were 6 and 8, respectively. It was acceptable that esterified PFAD was slightly below neutral, due to the probability of leaching active species (H<sub>2</sub>SO<sub>4</sub>) from solid acid catalyst prepared from rice husk, which contributes to the acidity. Therefore the utilisation of solid base catalyst was believed to be more effective in reducing the acidity of biodiesel (Zhang *et al.*, 2006).

#### 4.5.3 Calorific value analysis

Calorific value test for PFAD biodiesel was also performed to determine the properties of the biodiesel using Oxygen Bomb Calorimeter instrument. The results are observed and recorded as below. Calorific value (CV) is where the amount of heat release from the complete combustion over of the fuel weight and measured. The energy content of the fuel is measured in unit MJ/kg. The CV value of B100 biodiesel from PFAD (Table 4.7 ii) was 39.35 MJ/kg, which was slightly higher than CV for soybean biodiesel (37.2 MJ/kg) (Van Gerpen, 2005) and was lower than commercial diesel fuel (45.67 MJ/kg). Biodiesel is commonly contain less energy than diesel fuel as biodiesel is denser than diesel fuel (Van Gerpen, 2005).

The CV of B5 PFAD (Table 4.7 iii) was 45.07 MJ/kg, which was comparable to the CV of commercial B5 biodiesel (45.53 MJ/kg). Both B5 PFAD and commercial B5 biodiesel have CV slightly lower than diesel fuel (45.67 MJ/kg), which is in accordance to the previous report (Van Gerpen, 2005).

Entry	Type of sample	Calorific value (MJ/kg)
i	Esterified PFAD (E PFAD)	39.68
ii	B100 PFAD	39.35
iii	B5 PFAD	45.07
iv	B5 Commercial	45.53
v	Diesel fuel commercial	45.67

Table 4.7: Higher heating value (HHV) of biodiesel

### 4.6 Combustion capability test

The optimised biodiesel (B100 PFAD biodiesel) was demonstrated on an alternative diesel engine (Megatech- Mark III) for combustion capability test (Fig 4.20a-b). Ethanol was initially introduced into the combustion chamber to achieve 400-500°C before B100 was introduced.

B100 PFAD was successfully combusted in diesel engine (Figure 4.20b). Bright orange flame with less smoke was released upon combustion of B100 PFAD. Bright orange flame indicated the high temperature in the combustion chamber. In contrast to diesel, normally black smoke was emitted as a result of incomplete combustion (Yao *et al.*, 2008). Less and odourless smoke during B100 PFAD combustion indicated sufficient and complete combustion of the engine. The ignition took place in 10-15 minutes for a complete combustion of 100 ml B100 PFAD.



Figure 4.20: Combustion test of B100 PFAD on alternative diesel engine a) B100 PFAD entering the chamber b) ignition of B100 PFAD

The performance of fuel using diesel combustion engine can be observed by the relationship of torque, load and revolution per minute (rpm). Torque is a measurement of force onto an object to move (Brain, 2000). High torque value is needed for moving heavy object and normally simplified as load (George, 2008). A relationship between torque and load was obtained (Figure 4.19a) at which torque was proportionally increased with the B100 PFAD loading. This observation indicated that the engine can operate up to the maximum load of 100 lbs using B100 PFAD.

Besides torque, the relationship between load and rpm can also be observed from the engine's performance (Figure 4.19b). Revolution per minute is defined as the frequency of the rotation per minute of the column in diesel engine (Suvo, 2014). The rpm was decreased when the load of B100 PFAD increased. This is because when the load was introduced to the engine and became heavier, high force (torque) was needed to endure the load, thus causing the rpm to decrease.



Figure 4.21: a) Torque vs Load graph b) RPM vs Load graph

### 4.7 International standard analysis on B100 PFAD and B5 PFAD biodiesel

B100 and B5 PFAD biodiesel were tested according to SIRIM QAS International, Shah Alam. B100 PFAD biodiesel was tested following MS 2008:2008 standard (Automotive Fuel-Palm Methyl Ester for Diesel Engine Requirements and Test Methods) while B5 PFAD biodiesel was tested based on MS 123:2011 standard (Diesel Fuel Specification Part 1: Euro 2M). The data analysis of both samples is shown in Appendix J.

Four tests (ester content, density, viscosity and acid value) were conducted on B100 PFAD biodiesel. The density of B100 PFAD was 883 kg/m<sup>3</sup>, which was in the range of the requirement and compliances with MS 2008:2008 standard. Meanwhile, the ester content, viscosity and acid value had surpassed the requirement standard ranges. This could be due to several factors including degradation of the biodiesel (Bouaid *et al.*, 2007).

Biodiesel was reported to have high biodegradation up to 80% in 20 days or more (Demirbas, 2007) without the presence of any additive. In contrast with diesel fuel, biodiesel degrades 2.5 times faster than diesel fuel because diesel fuel degrades 50% in more than 20 days in regular conditions. Several studies have been reported that degradation of biodiesel could be influenced by temperature, moisture and storage time (Bouaid *et al.*, 2007).

B100 PFAD biodiesel gave slightly lower ester content (82.9%) than the minimum value requirement (96.5%) needed. This indicated on the possible degradation of B100 PFAD biodiesel *via* oxidation process after storage in a long period of time (>3 months) (Bouaid *et al.*, 2007). The esters in B100 PFAD could be converted into other compounds such as carboxylic groups (Wu *et al.*, 2011). The decreasing on ester content was also reported in previous study due to degradation of biodiesel from vegetable and used cooking oil after a long storage time (Bouaid *et al.*, 2007). Similar studies on degradation of biodiesel over time on sunflower, soybean and peanut oil were also reported (Wu *et al.*, 2011).

Acid value of B100 PFAD (8.53 mgKOH/g) tested by SIRIM was also surpassed the requirement range due to degradation of the sample prepared. The value was differed from previous test (Section 4.5.2), which gave the value of 0.49 mgKOH/g. The increase in acid value of B100 PFAD was due to the possibility of degradation on the oil whereby caused by the increment of carboxylic group or other compounds from oxidation process (Wu *et al.*, 2011). The utilisation of antioxidant as additive in biodiesel could prevent oxidation and also degradation (Bouaid *et al.*, 2007).

B5 PFAD (5% B100 PFAD biodiesel + 95% diesel fuel) was also analysed according to SIRIM QAS International, Shah Alam. B5 PFAD biodiesel was tested for 16 different tests. The acid number value obtained from B5 PFAD biodiesel (0.49 mgKOH/g) was slightly exceeding the requirement limit (0.25 mgKOH/g). This could be due to the degradation after long storage in SIRIM (similar to B100 PFAD).

## 4.8 Conclusion

In this study, silica from rice husk was successfully obtained. Base and acid heterogeneous catalysts were produced *via* impregnation step for both white and grey rice husk ash. The employment of the prepared solid acid catalyst (both WSAC and GSAC) in esterification of PFAD has successfully converted FFA into ester producing liquid esterified PFAD. The optimum parameters of esterification reaction was ratio 1:1 (MeOH:PFAD) with 5 wt% catalyst loading in 2 h reaction time. The esterified PFAD was successfully converted into complete PFAD biodiesel *via* transesterification reaction. Prepared solid base catalyst was employed in transesterification reaction with the optimum ratio 1:1 (MeOH:esterified PFAD) and 1 wt% catalyst loading in 30 min. Both utilisation of the prepared acid and base catalyst from rice husk contributed to high yield of biodiesel.

PFAD biodiesel is potentially used as an alternative to diesel fuel following successful demonstration of B100 PFAD onto diesel engine. Based on the performance of 4 different type of catalysts in transesterification, both WSBC and GSBC developed from RHA gave better yield of biodiesel in a shorter time compared to CaO and NaOH (WSBC/GSBC>CaO>NaOH). Based on the test results obtained from SIRIM, PFAD biodiesel underwent degradation in which contributes to several surpassed value.

Intensives precautions on storage time, environment temperature and addition of additives are suggested to prevent degradation process of biodiesel.

#### **CHAPTER 5**

#### **CONCLUSION AND RECOMMENDATION**

In this study, CaO was obtained from mussel shell and used in producing biodiesel from PFAD. Thick and highly viscous oil was produced for direct-transesterification of PFAD. New silica-based heterogeneous catalyst was studied using rice husk. Silica from rice husk ash (RHA) was successfully obtained and chemically activated to form solid base catalyst (SBC) and solid acid catalyst (SAC). Two types of RHA were produced upon calcination (white and grey) and to produce solid base (WSBC and GSBC) and acid (WSAC and GSAC) catalysts. WSAC and GSAC were employed in esterification reaction of PFAD, followed by transesterification reaction in the presence of base catalyst (WSBC, GSBC and CaO) to produce biodiesel.

The silica-based catalysts from rice husk ash gave excellent biodiesel conversion of >90% yield. In summary, the optimum parameters for esterification reaction using WSAC and GSAC was 1:1 (MeOH:PFAD) with 5 wt% catalyst in 2 h. The porosity and surface area of GARHA had effected the developed of GSAC as GSAC gave higher yield of esterified PFAD from WSAC. Meanwhile, the optimum parameters for transesterification reaction of esterified PFAD was 1:1 (MeOH:esterified PFAD) with 1 wt% catalyst amount in 30 min. Both of the white and grey solid base catalysts (WSBC & GSBC) showed higher catalyst efficiency than prepared CaO and NaOH.

B100 PFAD biodiesel showed excellent result on combustion test using the alternative diesel engine. Further analyses based on MS 2008:2008 and MS 123:2011 standards on

B100 PFAD and B5 PFAD showed that both biodiesel experienced fuel degradation as resulting from long storage and temperature changes during shipment and transportation. The degradation of the biodiesel contributes to higher viscosity, higher acid value and lower ester content.

In conclusion, this study has successfully developed green catalyst from agricultural waste. Furthermore, utilising PFAD from palm oil waste as biodiesel feedstock has contributed to green environment and waste management system.

Further recommendation study could be carried out to improve the preparation of the catalysts in terms of its binding strength and reusability, which could further reduce the production cost. Besides that, intensive precaution should be taken to prevent the degradation of the biodiesel. Addition of preservatives into the biodiesel able to prolong the shelf life of biodiesel and reduce biodiesel degradation.

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# **APPENDIX A**



Appendix A1: EDX spectra for CaO from mussel

ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.6638

Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
СК	0.277	8.77	0.11	16.65				14.5239
O K	0.525	36.73	0.74	52.34				42.6561
Ca K	3.690	54.50	1.39	31.01				147.6902
Total		100.00		100.00				



ZAF Method Sta	Indardle	ss Quant	itative	Analysis				
Fitting Coeffi	cient :	0.4479						
Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
СК	0.277	21.56	1.10	32.49				3.1612
O K	0.525	34.87	0.73	39.44				32.7584
Si K	1.739	43.56	0.27	28.07				64.0805
Total		100.00		100.00				



ZAF Method S	Standardle	ss Quant	itative	Analysis				
Fitting Coef	ficient :	0.4747						
Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
СК	0.277	28.41	0.88	40.37				5.6094
O K	0.525	35.11	0.75	37.46				34.7679
Na K								
Si K	1.739	36.48	0.27	22.17				59.6228
Total		100.00		100.00				

Appendix A4: EDX spectra for WSBC



ZAF Method Sta	ndardle	ss Quant	itative	Analysis				
Fitting Coeffi	cient :	0.5994						
Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
СК	0.277	29.98	1.21	41.80				6.6710
0 K	0.525	36.39	1.12	38.09				37.3208
Na K	1.041	0.40	0.57	0.29				0.5565
Si K	1.739	33.22	0.40	19.81				55.4517
Total		100.00		100.00				

Appendix A5: EDX spectra for WSAC



ZAF Method Standardless Quantitative	Analysis
--------------------------------------	----------

Fitting Co	pefficient :	0.4204						
Element	(keV)	Mass%	Error%	Atom%	Compound	Mass%	Cation	K
СК	0.277	19.20	1.19	29.41				2.5826
O K	0.525	36.21	0.73	41.64				33.8719
Na K	-	-	-	-				
Si K	1.739	41.34	0.28	27.08				59.4241
S K	2.307	3.25	0.33	1.87				4.1214
Total		100.00		100.00				
### **APPENDIX B**

Appendix B1: Acid value of PFAD, AV

 $\frac{N_{KOH} x MW_{KOH} x V_t}{W} = \frac{0.1 x 56.11 x 13}{0.4 g} = 182.36 mgKOH/g$ 

FFA% content= 182.36/2 = 91.18%

Appendix B2: Acid value of esterified PFAD, AV

 $\frac{N_{KOH} \times MW_{KOH} \times V_t}{W} = \frac{0.1 \times 56.11 \times 0.3}{0.28 \text{ g}} = 6.01 \text{ mgKOH/g}$ 

FFA% content= 6.01/2 = **3.01%** 

Appendix B3: Acid value of B100 PFAD biodiesel

 $\frac{N_{KOH} \times MW_{KOH} \times V_{t}}{W} = \frac{0.1 \times 56.11 \times 0.04}{0.46 \text{ g}} = 0.49 \text{ mgKOH/g}$ 

FFA% content= 0.49/2 = **0.25%** 

## **APPENDIX C**

# Appendix C1: BET result for WRHA

I	<u>Quantachro</u> © 1	meÆ ASiQwinō- A Acquisition 994-2011, <u>Quant</u> versi	utomated Gas Sorptio and Reduction <u>achrome</u> Instruments on 2.01	n Data
Analysis Operator: Sample ID: Sample Desc:	1 Date RICE HUSK ASH C1	:2014/06/09 Filename: Comment:	Report Operator: 1 RICE HUSK <u>Cl.gps</u> NURFARAHEN	Date:2014/06/11
Sample Weight: Approx. Outgas Analysis gas: Analysis Time:	0.0908 g Time:7.8 hrs Nitrogen 1:14 hr:min	Instrument: Final Outgas T Non-ideality: Bath temp.:	Autosorb iQ Station emp.:350 ∞C 6.58e-05 1/mmHg 77.35 K	1 Extended info: Available CellType: 6mm
Analysis Mode: VoidVol. Mode:	Standard He Measure	Cold Zone V: Data Reducti	1.47786 cc on Parameters	VoidVol Remeasure:on Warm Zone V: 7.74747 cc
	Thermal Transpirati	on: onEff. mol.	diameter (D): 3.54	≈Eff. cell stem diam. (d): 4.0000 mm
Adsorbate	Nitrogen <u>Molec</u> . Wt.: 28.013	Temperatu Cross Sec	re 77.350K tion: 16.200 ≈≤	Liquid Density: 0.808 g/cc
Re	lative	Volume	@ STP	1 / [ W((Po/P) - 1) ]
Pro	essure P/Po	cc/	g	
	1.00631e-01	0.	3644	2.4567e+02
	2.00920e-01	0.	4959	4.0572e+02
	4.01054e-01	0.	7423	7,2176e+02
	5.00847e-01	0.	8222	9.7643e+02
		в	ET summarv	
		Slope	= 1776.338	
		Intercept	= 4.347e+01	
	Correlation	coefficient, r	= 0.992092	
		C constant	= 41.863	
		Surface Area	= 1.914 m≤/g	
		Total Pore Total Pore	Volume summary Volume	
	Tota pores	al pore volume smaller than at P/Po =	= 5.161e-04 cc/g 7.8 ≈ (Radius) 0.09849	for

### Appendix C2: BET result for WARHA

#### Quantachrome& AS10wino- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01 Analysis Report Operator: 1 ACTIVATED RHA <u>C2.gps</u> Date:2014/06/09 Date:2014/06/11 Operator: 1 ACTIVATED RHA C2 Sample ID: Filename: Sample Desc: NURFARAHEN Comment: Instrument: <u>Autosorb</u> iQ Station 1 Final Outgas Temp.:350 ∞C Ex Non-ideality: C.C. Sample Weight: 0.0607 g Approx. Outgas Time:7.8 hrs Extended info: Available Extended CellType: Analysis gas: Nitrogen Analysis Time: 2:07 hr:min Analysis Mode: Standard Non-ideality: 6.58e-05 1/mmHg 6mm Bath temp.: 77.35 K VoidVol Remeasure:on Warm Zone V: 7.93358 cc VoidVol. Mode: He Measure Cold Zone V: 1.35873 cc Data Reduction Parameters Thermal Transpiration: onEff. mol. diameter (D): 3.54 ≈Eff. cell stem diam. (d): 4.0000 mm Adsorbate Nitrogen Temperature 77.350K Cross Section: 16.200 ≈≤ Molec. Wt.: 28.013 Liquid Density: 0.808 g/cc Volume @ STP 1 / [ W((Po/P) - 1) ] Relative Pressure P/Po cc/g 9.96143e-02 5,0897 1.7392e+01 1.99455e-01 6.1267 3.2538e+01 3.00018e-01 6.9211 4.9550e+01 3.99496e-01 7.6845 6.9269e+01 4.99493e-01 8.5975 9.2876e+01 BET summary Slope = 187.724 -3.920e+00 Intercept = Correlation coefficient, r = 0.995999 C constant= -46.888 18.947 m≤/g Surface Area =

Total Pore Volume summary Total Pore Volume

Total pore volume = 8.109e-03 cc/g for pores smaller than 7.8 ≈ (Radius) at P/Po = 0.09887

### Appendix C3: BET result for WSBC

Analysis

QuantachromeÆ ASiQwinô- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01 Report Date:2014/06/09 Operator: 1 SOLID BASE <u>C3.gps</u> Operator: 1 SOLID BASE C3 Sample ID: Sample Desc: Filename: NURFARAHEN Comment: Instrument: <u>Autosorb</u> iQ Station 1 Final Outgas Temp.:350 ∞C Ex Sample Weight: 0.0809 g Extended info: Available Approx. Outgas Time:7.8 hrs Analysis gas: Nitrogen Analysis Time: 1:52 hr:min Analysis Mode: Standard Non-ideality: 6.58e-05 1/mmHg 77.35 K Bath temp.:

VoidVol Remeasure:on Warm Zone V: 8.30058 cc VoidVol. Mode: He Measure Cold Zone V: 5.0473 cc Data Reduction Parameters Thermal Transpiration: onEff. mol. diameter (D): 3.54 ≈Eff. cell stem diam. (d): 4.0000 mm Nitrogen 77.350K Adsorbate Temperature Molec. Wt.: 28.013 Cross Section: 16.200 ≈≤ Liquid Density: 0.808 g/cc Relative Volume @ STP 1 / [ W((Po/P) - 1) ] Pressure P/Po cc/g 3.2053 1.01039e-01 2.8057e+01 1.99373e-01 3.9892 4.9947e+01 2.99365e-01 4.6327 7.3796e+01 9.2718e+01 1.2571e+02 4.00459e-01 5.7641 5.01552e-01 6.4046 BET summary 237.621 Slope = Intercept = 2.674e+00 Correlation coefficient, r = 0.996238 C constant= 89.878 14.493 m≤/g Surface Area =

Date:2014/06/11

6mm

CellType:

Total Pore Volume summary Total Pore Volume

Total pore volume = 4.985e-03 cc/g for pores smaller than 7.8 ≈ (Radius) at P/Po = 0.10041

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#### Appendix C4: BET result for WSAC

#### QuantachromeÆ ASiQwinô- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01 Analysis Report Date:2014/06/10 Date:2014/06/11 Operator: 1 Operator: 1 SOLID ACID C4. qps SOLID ACID C4 Sample ID: Filename: Sample Desc: Comment: NURFARAHEN Instrument: Autosorb iQ Station 1 Final Outgas Temp.:350 ∞C Ex Sample Weight: 0.0535 g Instrument: Extended info: Available Approx. Outgas Time:7.8 hrs Analysis gas: Nitrogen Analysis Time: 1:39 hr:min Non-ideality: 6.58e-05 1/mmHg CellType: Bath temp.: 77.35 K Analysis Mode: Standard VoidVol Remeasure:on Cold Zone V: 1.51083 cc VoidVol. Mode: He Measure Warm Zone V: 7.76395 cc Data Reduction Parameters Warm Lone V: 7.76395 CC Thermal Transpiration: onEff. mol. diameter (D): 3.54 =Eff. cell stem diam. (d): 4.0000 mm Adsorbate 77.350K Nitrogen Temperature Molec. Wt.: 28.013 Cross Section: 16.200 ≈≤ Liquid Density: 0.808 g/cc Relative Volume @ STP 1 / [ W((Po/P) - 1) ] Pressure P/Po cc/g 1.01329e-01 1.9143 4.7128e+01 2.00603e-01 2.2797 8.8074e+01 1.3117e+02 3.00840e-01 2.6246 4.00694e-01 2.9804 1.7949e+02 5.00813e-01 2.4121e+02 3.3279 BET summary Slope = 480.067 Intercept = -7.016e+00 Correlation coefficient, r = 0.996418 C constant= -67.424 Surface Area = 7.362 m≤/g Total Pore Volume summary Total Pore Volume

Total pore volume = 2.726e-03 cc/g for pores smaller than 7.8 ≈ (Radius) at P/Po = 0.09865

### Appendix C5: BET result for GRHA

#### Quantachrome& ASiQwing- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01 Analysis Report Operator: 1 Date:2015/02/25 Operator: 1 Date:2015/03/06 Filename: PRHA.gps Comment: NURFARAHEIN Instrument: Autosorb iQ Station 1 Final Outgas Temp.:350 °C Ex PRHA Sample ID: Sample Desc: Sample Weight: 0.12 g Approx. Outgas Time:7.8 hrs Extended info: Available Analysis gas: Nitrogen Analysis Time: 2:30 hr:min Non-ideality: 6.58e-05 1/mmHg CellType: 6mm w∕o rod Bath temp.: 77.35 K Analysis Mode: Standard VoidVol. Mode: He Measure VoidVol Remeasure:on Warm Zone V: 8.01773 cc Cold Zone V: 1.22438 cc Data Reduction Parameters Thermal Transpiration: onEff. mol. diameter (D): 3.54 ==Eff. cell stem diam. (d): 4.0000 mm Temperature 77.350K Cross Section: 16.200 ≈≤ Nitrogen Adsorbate Molec. Wt.: 28.013 Liquid Density: 0.808 g/cc Relative Volume @ STP 1 / [ W((Po/P) - 1) ] Pressure P/Po cc/g 1.00828e-01 17.4489 5.1420e+00 1.99843e-01 20.7141 9.6473e+00 2.99076e-01 23.8806 1.4296e+01 27.6542 4.00654e-01 1.9341e+01 BET summary 47.314 Slope = 2.735e-01 0.999799 Intercept = Correlation coefficient, r = C constant= 174.008 Surface Area = 73.182 m≤/g Total Pore Volume summary Total Pore Volume

Total pore volume = 2.831e-02 cc/g for pores smaller than  $7.8 \approx (\text{Radius})$ at P/Po = 0.10079

## Appendix C6: BET result for GARHA

#### Quantachrome& ASiQwinô- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01

Analysis			Report		
Operator:	1 Dat	e:2015/02/24	Operator: 1	Date	2015/03/06
Sample ID:	PARHA	Filename:	PARHA. qps		
Sample Desc:		Comment:	NURFARAHEIN		
Sample Weight:	0.0849 g	Instrument:	Autosorb iQ Station	1	
Approx. Outgas	Time:7.8 hrs	Final Outgas T	emp.:350 ∞C	Extended info:	Available
Analysis gas:	Nitrogen	Non-ideality:	6.58e-05 1/mmHg	CellType:	6mm w/o rod
Analysis Time:	2:39 hr:min	Bath temp.:	77.35 K		
Analysis Mode:	Standard			VoidVol Remeasu	ure:on
VoidVol. Mode:	He Measure	Cold Zone V:	1.25721 cc	Warm Zone V:	8.00253 cc
		Data Reducti	on Parameters		
	Thermal Transpirat	ion: onEff. mol.	diameter (D): 3.54 =	≈Eff. cell stem	diam. (d): 4.0000 mm
Adsorbate	Nitrogen	Temperatu	re 77.350K		
	Molec. Wt.: 28.013	Cross Sec	tion: 16.200 ≕≤	Liquid Density	: 0.808 g/cc
Re	lative	Volume (	@ STP	1 / [ W((Po/P)	- 1) ]
	P/Po	ccl	9		
	1710	007	a		
	1.00291e-01	29.	3430	3.0390	5e+00
	2.00735e-01	35.	0887	5.726	9e+00
	3.00618e-01	40.	5685	8.477	5e+00
	4.00835e-01	46.	3772	1.1542	2e+01
		В	ET summary		
		Slope	= 28.214		
		Intercept	= 1.254e-01		
	Correlation	coefficient, r	= 0.999509		
		C constant	= 225.950		
		Surface Area	= 122.887 m≤/g		
		Total Pore	Volume summary		
		Total Pore	Volume		

Total pore volume = 4.638e-02 cc/g for pores smaller than  $7.8 \approx$  (Radius) at P/Po = 0.10020

### Appendix C7: BET result for GSBC

#### Quantachrome& ASiQwing- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01 Analysis Report Operator: Date:2015/02/25 Operator: 1 Date:2015/03/06 1 Filename: PSBC.qps Comment: NURFARAHEIN Instrument: Autosorb 10 Station 1 Final Outgas Temp.:350 oc Ex Sample ID: PSBC Sample Desc: Sample Weight: 0.1399 g Approx. Outgas Time:7.8 hrs Extended info: Available Non-ideality: 6.58e-05 1/mmHg Bath temp.: 77.35 K Analysis gas: Nitrogen Analysis Time: 1:31 hr:min Analysis Mode: Standard CellType: 6mm w/o rod VoidVol Remeasure:on Warm Zone V: 7.74466 cc VoidVol. Mode: He Measure Cold Zone V: 6.47949 cc Data Reduction Parameters Thermal Transpiration: onEff. mol. diameter (D): 3.54 ≈Eff. cell stem diam. (d): 4.0000 mm Adsorbate Nitrogen 77.350K Temperature Molec. Wt.: 28.013 Cross Section: 16.200 ≈≤ Liquid Density: 0.808 g/cc 1 / [ W((Po/P) - 1) ] Relative Volume @ STP Pressure P/Po cc/g 1.00016e-01 0.3971 2.2395e+02 2.01607e-01 0.1141 1.7713e+03 3.01173e-01 -0.0402 -8.5714e+03 4.00915e-01 -0.2485 -2.1544e+03 BET summary Slope = -17419.805 2.188e+03 Intercept = Correlation coefficient, r = 0.494846 C constant= -6.960 Surface Area = 0.000 m≤/g Total Pore Volume summary Total Pore Volume

Total pore volume = -5.346e-05 cc/g for pores smaller than 7.8 ≈ (Radius) at P/Po = 0.09909

# Appendix C8: BET result for GSAC

#### Quantachrome& ASiQwinô- Automated Gas Sorption Data Acquisition and Reduction © 1994-2011, Quantachrome Instruments version 2.01

Analysis		F	Report		
Operator:	1 Dat	e:2015/02/27 0	perator: 1	Date:2015/	/03/06
Sample ID:	PSAC	Filename: P	SAC.qps		
Sample Desc:		Comment:	URFARAHEIN		
Sample Weight:	0.059 g	Instrument: A	utosorb iQ Station	1	
Approx. Outgas	Time:7.8 hrs	Final Outgas Tem	np.:350 ∞C	Extended info: Avail	lable
Analysis gas:	Nitrogen	Non-ideality: 6	5.58e-05 1/mmHg	CellType: 6mm v	v∕o rod
Analysis Time:	2:14 hr:min	Bath temp.: 7	7.35 K		
Analysis Mode:	Standard			VoidVol Remeasure:or	1
VoidVol. Mode:	He Measure	Cold Zone V: 0	.858494 cc	Warm Zone V: 8.060	002 cc
		Data Reduction	Parameters		
	Thermal Transpirat	ion: onEff. mol. d	liameter (D): 3.54	≈Eff. cell stem diam.	(d): 4.0000 mm
Adsorbate	Nitrogen	Temperature	77.350K		
	Molec. Wt.: 28.013	Cross Secti	ion: 16.200 ≈≤	Liquid Density: 0.80	08 g/cc
Rel	lative	Volume @	STP	1 / [ W((Po/P) - 1)	]
Pre	essure				
F	P/Po	cc/g			
	9.93060e-02	17.12	261	5.1510e+00	
	2.01316e-01	20.79	950	9.6984e+00	
	3.01894e-01	23.64	144	1.4634e+01	
	4.00885e-01	26.84	185	1.9941e+01	
		BET	summary		
		Slope =	49.031		
		Intercept =	5.665e-02		
	Correlation	coefficient, r =	0.999153		
		C constant=	866.526		
		Surface Area =	70.946 m≤/g		

## **APPENDIX D**

Appendix D1: Esterified PFAD yield using WSAC

Percentage yield,  $\% = \frac{18.32 \text{ g}}{20.00 \text{ g}} \times 100\% = 91.6\%$ 

Appendix D2: Esterified PFAD yield using GSAC

Percentage yield, % =	<u>18.60 g</u>	x 100%	=	93.0%
	20.00 g			

## **APPENDIX E**



Appendix E1: GCMS chromatogram of PFAD

Appendix E2: GCMS chromatogram of esterified PFAD





# Appendix E3: GCMS chromatogram of B100 PAFD biodiesel

### **APPENDIX F**



Appendix F1: FTIR spectrum of using 5 wt% WSBC

Appendix F2: FTIR spectrum of B100 PFAD biodiesel



# **APPENDIX G**

Reaction time (min)	WSBC (1 wt%)	GSBC (1 wt%)	CaO (1 wt%)	CaO (5 wt%)
15	97.95	97.43	96.70	96.70
30	99.73	99.46	96.27	96.48
45	99.65	99.23	96.27	96.48
60	99.57	99.48	96.27	96.58

Appendix G1: Biodiesel conversion yield (%)

# **APPENDIX H**

Reaction time (min)	WSBC (1 wt%)	GSBC (1 wt%)	CaO (1 wt%)	CaO (5 wt%)
15	12.5	12.5	0.0	1.0
30	21.0	19.0	0.0	3.0
45	20.0	19.2	0.0	8.0
60	20.0	19.0	0.5	9.0
90	20.0	19.0	0.8	12.0
24 h			1.0	13.0

Appendix H1: Percentage weight of glycerol produced

# **APPENDIX I**

# Appendix I1: Calorific value of esterified PFAD

T. Charles and a characteristic structure and a structure of the structure os structure of the structure os structure of the structure os st	anning cranter or surprise		
The delta T fo	r the curr		
ac avraadad th	a costiaur	ent ru	11 (11.001)   
(may) /This	e cuntigor	eu lim.	11 07 11.000
AmdX/. (IIIIS	is only a	Warnin	g - the run
nas completed	SUCCESSIUL	Ly)	
Parr 6400 Calo	rimeter R	ev. 10	1227170111
	poor .	/04/14	04:14:20
Mode: Determin	ation		
Method: Dy	namic Tupe	a Pi	reliminaru
Sample ID: EST	ERFARAHEN		
Bomb ID	1 EE V	alue	940.0000
Weight - 1	.0929 Spik	e Woht	0.0000
Fuse 50	.0000 Acid		8.0000
Sulfur 0	.0000		
Init. Temp 30.	.1316 Temp.	. Rise	11.0811
Jacket T 30	.0573		
	Gross	s Heat	39.6813
			MT/LA

Appendix I2: Calorific value of B100 PFAD

		WATER IS NOT BEEN IN	-
A Misfire c	andition	has been det	ected.
In error or	annafille	167W(10251CD)	MINAMA
The delta T	for the	current run	(10.244) h
as exceeded	the high	n warning set	point of
8.500. (Thi:	s is only	, a warning -	the run h
as complete	d success		
	alorimete	er Rev. 1012	
		11/03/14	
Mode: Deter	mination		
Method:		Type: Pre	
Sample ID:	E2		
	29.6454	Temp. Rise	10.2438
Jacket T	30.0489		
		Gross Heat	39.3523
			MJ/kg

# Appendix I3: Calorific value of B5 PFAD

Annual Annual Annual			E SIE	
the delta	tor the	curre	nt rur	(11.929)
as exceeded	i the con	figure	d limi	t of 11.00
(max). (T)	nis is on	ly a w	arning	- the run
has complet	led succe	ssfull	4)	
Parr 6400 (	alorimet	er Re	v. 101	227170111
		11/	04/14	03:14:29
Mode: Deter	mination			
Method:	Dunamic	Tune:	Pr	eliminaru
Sample ID:	BSFARAHFI	N		a a a marrar ag
Bomb ID	1	FF Va	lue	940,0000
Bomb ID Weight	1.0364	EE Val Snika	lue Nobt	940.0000
Bomb ID Weight Fuce	1.0364	EE Va Spike Ocid	lue Wght	940.0000 0.0000
Bomb ID Weight Fuse	1 1.0364 50.0000	EE Va Spike Acid	lue Wght	940.0000 0.0000 8.0000
Bomb ID Weight Fuse Sulfur Init Tons	1.0364 50.0000 0.0000	EE Va Spike Acid	Wght	940.0000 0.0000 8.0000
Bomb ID Weight Fuse Sulfur Init. Temp	1 1.0364 50.0000 0.0000 30.0649	EE Va Spike Acid Temp.	lue Wght Rise	940.0000 0.0000 8.0000 11.9294
Bomb ID Weight Fuse Sulfur Init. Temp Jacket T	1 1.0364 50.0000 0.0000 30.0649 30.0294	EE Val Spike Acid Temp.	lue Wght Rise	940.0000 0.0000 8.0000 11.9294

Appendix I4: Calorific value of commercial B5

This is a second second second second	Manufacture Construction of the Construction o
TIMESKANAM COURSES IN MUSER	初に留きていた時になった。
ine delta i for the curr	rent run (12.087) h
as exceeded the configur	ed limit of 11.000
(max). (This is only a	warning - the run
has completed successful	1y)
Parr 6400 Calorimeter R	ev. 101227170111
11	/04/14 02:59:22
Modet Determination	CYTLAT VATURAS
Hathada Dupania Tura	Constrained
nethod: Dynamic Type	r rreiiminary
Sample ID: RPCONNERCIAL	
Bond ID 1 EE V	alue 940.0000
Weight 1.0394 Spik	e Wght 0.0000
Fuse 50.0000 Acid	8.0000
Sulfur 0.0000	
Init. Temp 30.0112 Temp	. Rise 12,0849
Jacket T 29,9968	
Groc	- Hont AC 5707
orus	5 Hear 40.0010
	nu/.kg

# Appendix I5: Calorific value of diesel fuel

The delta T for the current run (12.019) h as exceeded the configured limit of 11.000 (max). (This is only a warning - the run has completed successfully) Parr 6400 Calorimeter Rev. 101227170111 11/04/14 02:44:43 Mode: Determination Method: Dynamic Type: Preliminary Sample ID: DIESELPETRONAS-1 Bomb ID 1 EE Value 940.0000
Parr 6400 Calorimeter Rev. 101227170111 11/04/14 02:44:43 Mode: Determination Method: Dynamic Type: Preliminary Sample ID: DIESELPETRONAS-1 Bomb ID 1 EE Value 940.0000
Mode: Determination Method: Dynamic Type: Preliminary Sample ID: DIESELPETRONAS-1 Bomb ID 1 EE Value 940.0000
Method: Dynamic Type: Preliminary Sample ID: DIESELPETRONAS-1 Bomb ID 1 EE Value 940.0000
Sample ID: DIESELPETRONAS-1 Bomb ID 1 EE Value 940.0000
Bomb ID 1 EE Value 940.0000
0 1 2
Weight 1.0304 Spike Wight 0.0000
Fuse 50.0000 Acid 8.0000
Sulfur 0.0000
Init. Temp 29,8597 Temp, Rise 12,0194
Jacket T 29,9912
Gross Heat 45.6724 MJ/kg

## **APPENDIX J**

# Appendix J1: SIRIM test for B100 PFAD

Selangor Darul I Tel. no: 03-554 Fax. no: 03-554 www.sirim-qas.c	Ehsan, Malaysia 46651/55446658 46688 oom.my TEST F	REPORT
REPORT NO. : 2014CE		PAGE: 1 OF 2
This Test Report refers only to s International Sdn. Bhd. This test forms (including but not limited to Sdn. Bhd. Please refer overleaf or	samples submitted by the applic report shall not be reproduced, o advertising purposes) without to f Page 1 for Conditions Relating	ant to SIRIM QAS International Sdn. Bhd. and tested by SIRIM QA except in full and shall not be used for any purpose by any means written approval from the Managing Director, SIRIM QAS Internation To The Use of Test Report
Applicant/Manufacturer	: UNIVERSITI MALA 94300 Kota Samara Sarawak, Malaysia (Dr. Zainab Ngaini) (Ms. Nurfarahen Ja	YSIA SARAWAK (UNIMAS) ahan, mil)
Product	: Oil	
Reference standard / Method of test	: MS 2008:2008 Automotive Fuels - Requirements and	Palm Methyl Ester (PME) for Diesel Engines – Test Methods
Description of sample	: Received one (1) s which was marked Marking : Sample	sample of <b>oil</b> described as <b>BIODIESEL</b> for testir as: 4
Date received of complete application	: 16 October 2014	
Job No.	: J20141401345	
Overall Test Result	The test results for report are describe	the <mark>su</mark> bmitted test samples as described in this te d in next pages.
Issued date	: 18 November 2014	
Approved Signatory	Augoool	
(MUHAMMAD NURI Testing I IKM A/332	DIN GHAZALI, AM/C) Executive 25/6168/12	(HAHNAS MAHBUT) Head, Chemical & Consumer Section (CEST), Testing Services Department.

#### REPORT NO. : 2014CE1473

PAGE: 2 OF 2

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#### **Test Results**

Sample : BIODIESEL Marking : Sample 4

No.	Type of Tests	Requirements MS 2008: 2008	Results	Remarks
1.	Ester Content, % (m/m) (EN 14103)	96.5 (minimum)	82.9	Fail
2.	Density at 15 °C, kg/m3 (ASTM D4052)	860 to 900	883	Pass
3.	Viscosity at 40 °C, mm2/s (MS 1831)	3.50 to 5.00	6.047	Fail
4.	Acid Value, mg KOH/g (MS 2011)	0.50 (maximum)	8.53	Fail
Notes:	(<) less than	-	$\frown$	

(-) indicates negative

Needer niese

MUHAMMAD NURDIN GHAZALI, AMIC (TKM A/3325 '6168/12) Testing Executive Chemical & Consumer Section SIRIM QAS International Sdn. Bhd.

# Appendix J2: SIRIM test for B5 PFAD

TEST REPORT				
	-1474	PAGE: 1 OF 2		
This Test Report refers only to s International Sdn. Bhd. This test forms (including but not limited th Sdn. Bhd. Please refer overleaf of	amples submitted by the applic report shall not be reproduced, o advertising purposes) without f Page 1 for Conditions Relating	by the applicant to SIRIM QAS International Sdn. Bhd. and tested by SIRIM QA reproduced, except in full and shall not be used for any purpose by any means ses) without written approval from the Managing Director, SIRIM QAS Internation ions Relating To The Lies of Test Paport		
Applicant/Manufacturer	: UNIVERSITI MALAYSIA SARAWAK (UNIMAS) 94300 Kota Samarahan, Sarawak, Malaysia. (Dr. Zainab Ngaini) (Ms. Nurfarahen Jamil)			
Product	: Oil			
Reference standard / Method of test	: MS 123:2011 Diesel Fuel - Spec	fication – Part 1: Euro 2M.		
Description of sample	Received one (1) which was marked Marking : Sample	sample of <b>oil</b> described as <b>BIODIESEL</b> for testi as: 2		
Date received of complete application	: 16 October 2014			
Job No.	: J20141401346			
Overall Test Result	The test results for report are describe	the submitted test samples as described in this te d in next pages.		
Issued date	: 18 November 2014			
Approved Signatory	atuesee			
(MUHAMMAD NURE Testing E IKM A/332	DIN GHAZALI, AMIC) Executive 25/6168/12	(UU) (HAHNAS MAHBUT) Head, Chemical & Consumer Section (CEST), Testing Services Department.		

REPORT NO. : 2014CE1474

PAGE: 2 OF 2

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**Test Results** 

Sample : BIODIESEL Marking : Sample 2

Remark : Sample 2 was mixed with Petro Diesel to form B5 Biodiesel

No.	Type of Tests	Requirements MS 123-1: 2011	Results	Remarks
1.	Colour (ASTM) (MS 2010)	2.5 (maximum)	L 1.0	Pass
2.	Ash, % mass (MS 2013)	0.01 (maximum)	0.002	Pass
3.	Flash Point, °C (MS 686)	60 (minimum)	71.0	Pass
4.	Kinematic Viscosity at 40°C, mm <sup>2</sup> /s (MS 1831)	1.5 to 5.8	3.578	Pass
5.	Copper corrosion (3 h at 100°C) (MS 787)	1 (maximum)	1a	Pass
6.	Water, % vol (MS 1800)	0.05 (maximum)	< 0.05	Pass
7.	Sediment by extraction, % mass (MS 790)	0.01 (maximum)	< 0.01	Pass
8.	Carbon Residue, mass % (MS 962)	0.20 (maximum)	0.07	Pass
9.	Density at 15°C, kg/l (MS 1893)	0.810 to 0.870	0.8527	Pass
10.	Acid Number, mg KOH/g (MS 2011)	0.25 (maximum)	0.49	Fail
11.	Electrical Conductivity, pS/m (MS 1889)	50 (minimum)	907	Pass
12.	Cetane Index (MS 1890)	49 (minimum)	51.0	Pass
13.	Distillation at 95 %, °C (MS 563)	370 (maximum)	363	Pass
14.	Total Sulphur, mg/kg (MS 1891)	500 (maximum)	280	Pass
15.	Lubricity, µm (MS 1892)	460 (maximum)	200	Pass
16.	Cloud Point, °C (ASTM D2500)	19.0 (maximum)	8	Pass
Notes	(<) less than		(	1

(-) indicates negative

MUHAMMAD NU DI (IKM A/3.2.2.6 12) Testing Focusion Chemical & Construction SIRIM QAS ... ter monor son. Bhd.