ALKALI AND RARE EARTH METALS LOADING ON DEOILED-SPENT BLEACHING CLAY AS CATALYSTS IN TRANSESTERIFICATION OF WASTE OILS

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DEDICATION

Dedicated to my parents, my husband and siblings, who support me with never-ending inspiration, everlasting supports and priceless encouragements towards the success of my degree.

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ABSTRACT

In the present work, waste source, namely deoiled spent bleaching clay (DSBC) loaded with K, Ca and La, have been successfully utilized as solid catalysts in the transesterification of refined, bleached and deodorized palm olein (RBD-PO), waste palm cooking oil (WPCO) and spent bleaching clay (SBC) oil to produce methyl esters (biodiesel). The triglycerides source from waste source such as WPCO and SBC can help to reduce the production cost and do not cause food issue. But these types of feedstocks have high moisture and free fatty acid (FFA) hence; we need to find a heterogeneous catalyst to overcome this. In order to enhance the catalytic activity, the deoiled SBC had been calcined at 500 ℃ for 10 h and doped with KOH, CaO and La_2O_3 using wet impregnation method. The catalysts were characterized with TGA, FTIR, XRD, XRF, BET, FESEM, ICP and Hammett indicators (phenolphthalein, 2,4-dinitroaniline and 4-nitroaniline). In the transesterification reaction, we found out that K-DSB gives the best yield. The best reaction conditions found to be: for transesterification of RBD-PO, WPCO and SBC oil using K-DSBC was 3 wt.% catalyst amount (based on oil weight) and 9:1 methanol to oil molar ratio for 2 h reaction period producing 98.9 % methyl ester yield. Meanwhile for the transesterification of WPCO and SBC oil require 3 h and 4 h reaction duration. All catalysts undergo transesterification at the reflux temperature of methanol (65 ℃). Furthermore, the regenerated of the catalytic activity was investigated, and found that all the three catalysts could be reused up to five times, while maintaining methyl esters content above 80%. In addition, the catalysts exhibit tolerance towards the presence of water at 1.75% and 2.0% and FFA at 1.75% and 1.75%, respectively, with over 80% of methyl esters content.

ABSTRAK

Dalam kajian ini, bahan buangan tanah liat pelunturan yang dibuang minyak dimasukkan dengan K, Ca dan La telah berjaya digunakan sebagai mangkin pejal dalam proses transesterifikasi menggunakan minyak sawit tulen (RBD-PO), minyak masak sawit terpakai (WPCO) dan minyak tanah liat pelunturan (SBC) bagi menghasilkan metil ester (biodiesel). Sumber minyak daripada bahan terbuang seperti WPCO dan SBC boleh membantu mengurangkan kos dan tidak menimbulkan isu terhadap pemakanan. Tetapi sumber ini mengandungi kadar air and lemak asid yang tinggi justeru memerlukan mangkin heterogen. Dalam usaha untuk meningkatkan aktiviti mangkin, tanah liat pelunturan yang telah dibuang minyak telah dikalsin pada suhu 500 ℃ selama 10 jam dan ditambah dengan KOH, CaO dan La_2O_3 dengan cara pengisitepuan basah. Kesemua mangkin diuji dengan menggunakan TGA, FTIR, XRD, XRF, BET, FESEM, ICP dan penunjuk Hammett (phenolphthalein, 2,4-dinitroaniline and 4-nitroaniline). Di dalam transesterifikasi reaksi, didapati K-DSBC memberikan keputusan terbaik. Keadaan terbaik tindak balas untuk transesterifikasi daripada RBD-PO menggunakan K-DSBC sebagai mangkin adalah 3% (berdasarkan berat minyak) dan 9:1 nisbah molar metanol kepada minyak, selama 2 jam menghasilkan 99.0% metil ester. Untuk transesterifikasi dengan menggunakan WPCO dan minyak SBC memerlukan 3 jam dan 4 jam masa reaksi. Kesemua mangkin menjalani transesterifikasi pada suhu refluks metanol (65 ℃). Keberkesanan penggunaan semula mangkin dikaji dan didapati bahawa ianya boleh digunapakai semula sebanyak 5 kali dengan kandungan metil ester lebih dari 80%. Tambahan pula, mangkin masing-masing menunjukkan toleransi terhadap air pada 1.75% dan 2.0 % dan asid lemak bebas pada 1.75% dengan kandungan metil ester lebih dari 80%.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
CPO	Crude palm oil
DOBI	Deterioration of bleachability index
DSBC	De-oiled spent bleaching clay
EDX	Energy dispersive X-ray
FAME	Fatty acid methyl esters
FE-SEM	Field emission-scanning electron microscope
FFA	Free fatty acids
GC-FID	Gas chromatography-flame ionization detector
GC-MS	Gas chromatographymass spectrometry
GHG	Greenhouse gases
ICP-MS	Inductively coupled plasma-mass spectrometry
ME	Methyl esters
MeOH	Methanol
O-SBC	Oil extracted from spent bleaching clay
PE	Petroleum ether
RBD-PO	Refined, bleached and deodourized-palm olein
SBC	Spent bleaching clay
TGA/DTA	Thermogravimetry analysis/differential thermal analysis
TLC	Thin layer chromatography
WPCO	Waste palm cooking oil
XRD	X-ray diffraction
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.1 Introduction

The global energy demand is increasing worldwide. Limited crude petroleum reserves are on the verge of reaching their peak production. The main cause is due to globally growth of industrialization and rapid human population growth at the same time. Global population is estimated to increase up to 30 % in the next 25 years, where the increase of 80 - 90 % is predictable to be in developing countries (IEA, 2004). Fossil fuel has becoming a vital energy source for many decades. This may lead to fossil fuel depletion where depletion of known petroleum reservoirs will make renewable energy sources more attractive. Hence, searching for alternatives to fossil fuels has attracted a worldwide interest in recent years in concerning the greenhouse gas emissions and instability of crude oil price.

As we can see from Figure 1.1, the usage of fossil fuel is high and demands by the world meanwhile other sources such as solar, wind, nuclear, geothermal and hydro is quite lesser as to be compared to coal, oil and gas. Hence, it is crucial to find an alternative source for fossil fuel considering the fossil fuel depletion and global warming issue. The alternative to fossil fuel is found out to be biodiesel. Biodiesel is also called as fatty acid methyl ester (FAME). In light of the fact that it is non-harmful, biodegradable and non-combustible, biodiesel picking up worldwide prevalence as an elective vigour source. Biodiesel have been attracted the attention since it lowers the emissions of carbon monoxide, greenhouse gases, unburned hydrocarbons, poly-aromatics, oxides of sulfur and particulate matters compared to conventional diesel. Due to that, biodiesel is being called as environmental friendly fuel. Likewise, the biodegradability lands of biodiesel make biodiesel as an eco-accommodating. It is a biodegrable and biorenewable fuel, made from eco-friendly resources such as vegetable oil, animal fat, used cooking oil, waste fats, algal oils and alcohol such as methanol or ethanol forming new ester and glycerol as a side product by a process called transesterification reaction. In other words, biodiesel is a mixture of alkyl esters of long chain fatty acids that is synthesized through transesterification or other process of triglycerides.

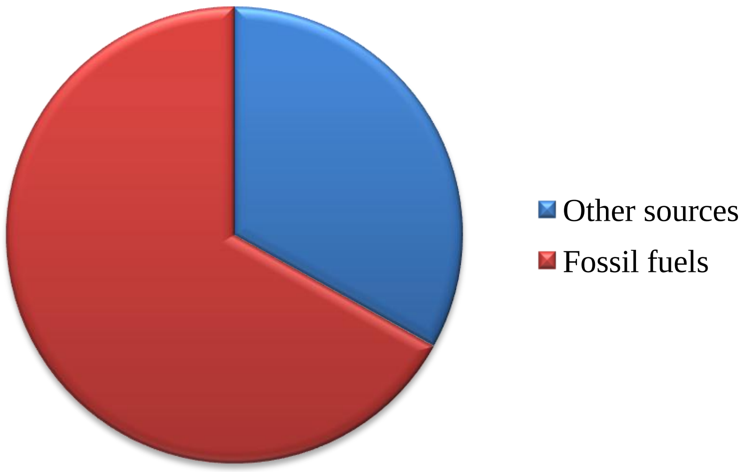


Figure 1.1 Fossil fuel usage

Source: EIA, MER, (2016)

Transesterification reaction can be carried out by both homogeneous (acids and alkalis) and heterogeneous catalysts. Catalyst is necessary to increase the rate of reaction and transesterification reaction conversion. Homogeneous catalysts applications is usually due to less time consumed and simple usage, thus, chosen by industry. Homogeneous catalysts act in the same liquid phase as the reaction mixture while heterogeneous catalyst; usually solid, act in different phase of reaction mixture. Heterogeneous catalytic system can produce high quality esters and glycerol (Taufiq-Yap et al., 2014).

Biodiesel is safe, renewable, biodegrable in water, non-toxic, has a high flash point and contains less sulfur compounds. We can prove that biodiesel has benefit in term of green environment with those reasons.

1.2 Problem Statement

Biodiesel production cost has been the main barrier for commercializing biodiesel recent years and the major contributor for this problem is the feedstock cost itself. The use of low cost oil for biodiesel production becomes very attractive and in this work, the feedstock that was sourced from waste oil is waste palm cooking oil (WPCO) meanwhile refined, bleached and deodorized palm olein (RBDPO) is obtained from local grocery. Other than that, the oil extracted from spent bleaching clay (SBC) was also being investigated as a new waste source of waste. The disposal of SBC has become increasingly unacceptable due to potential environmental hazards and the rising cost of disposal. This has prompted urgency in innovating practical and economical ways in utilizing SBC.

On the other hand, the waste oil is low in quality feedstock which will require a suitable catalyst to tolerance its moisture and FFA. This work involved the production of biodiesel also utilization waste sources as the catalyst. The catalyst derived from waste source (deoiled spent bleaching clay) which is cost effective with good availability. The oil from SBC will be extracted and utilized as a feedstock. Meanwhile the deoiled SBC (DSBC) was utilized as a catalyst support. Since SBC is a refinery waste, it could be utilized as a usable material because it has sufficient surface area and porosity. A solid catalyst is able to tolerate the moisture and fatty acid in the feedstock as well as can be recycled. By utilizing the waste matters, the cost of the production biodiesel could be minimized, and natural mineral resources could be utilized. The environment also can be protected through the pollution reduction and use of green technology. To remain competitive as petro-diesel, biodiesel feedstock must be available at lower price possible. Other properties of feedstock include low agriculture input, favourable fatty acid composition, high oil content and have potential market for agricultural by-products.

The utilization of oil and catalyst from waste sources could contribute to the improvement of environmental damage. Furthermore, many research works within last decade have focused on the exploitation of waste materials as feedstocks and catalysts for the production of biodiesel. This includes spent bleaching clay, decanter cake and palm fatty acid distillate for feedstocks whereas shells, ashes, rock, and bone for catalysts (Xie et al., 2009; Boey et al., 2011d; Ilgen, 2011, and Obadiah et al., 2012). Exploitation of such waste materials has becoming very attractive due to their high abundance and low cost. As such, this work is focusing on feedstock and catalyst from waste source in the preparation of methyl esters.

1.3 Research Objectives

In this study, solid derived from waste source was used as catalyst in transesterification of palm based oils to produce biodiesel. Hence, this study embarks on the following objectives:

1. To synthesize and characterize K, Ca and La loaded onto DSBC by wet impregnation and solid state synthesis methods.
2. To transesterify RBD-PO, WPCO and SBC oil using DSBC loaded with K, Ca and La.

1.4 Scope of Study

The potential of a new catalyst from alkali and rare earth metals onto deoiled-spent bleaching clay is being investigated and to convert RBD-PO, WPCO and SBC into biodiesel. The methods of catalyst synthesis are discussed in the methodology section. In this work, a novel approach is proposed where the DSBC is used as a catalyst support in the transesterification process. The SBC is used as a source of oil and extracted using Soxhlet and sonication method. The optimization of catalyst preparation method (wet impregnation) plays an important role in term of catalytic stability and activity.

Suitable solid catalyst must be used to transesterify waste oils. Catalyst is characterized using FTIR, TGA, XRD, XRF, BET and FESEM-EDX. Next, the factors that influence transesterification reaction of RBD-PO, WCO and O-SBC were optimized such as methanol to oil molar ratio (3:1 - 18:1), catalyst loading (1 wt.% - 12 wt.%) and reaction time (1 h – 24 h).

The feedstock (RBD-PO, WPCO and O-SBC) first undergoes the oil analysis prior to transesterfication reaction in order to investigate the properties such as density, viscosity and moisture content. Methyl esters obtained also proceed with the gas chromatography with both mass spectrometry and flame ionization detector for the qualitative and quantitative properties of oils. Methyl esters analysis testing done are cloud point, flash point, sulphur content and higher heating value.

CHAPTER 2

LITERATURE REVIEW

2.1 Biodiesel

Finding alternatives to fossil fuels has attracted a worldwide interest in recent years since the traditional fossil fuel resources are becoming limited. Increasing concerns about the potential of global climate change, declining air and water quality, and serious human health concern are inspiring the development of biodiesel, as a renewable, cleaner burning diesel alternative. The FAME, or also known as biodiesel, is regarded as the best substitute for conventional petro-based diesel fuel. The alternatives to diesel fuel must be technically feasible, economically competitive, environmental acceptable and readily available. The triglyceride satisfies all the requirements of diesel alternative. Indeed, vegetable oils are renewable and widely available from a variety of sources (Encinar et al., 2007). Even though properties of biodiesel are varying with the oil feedstock and the types of alcohol used, it can be utilized as direct substitute for traditional diesel fuel that satisfy the providing standard specifications.

Biodiesel could be the best substitute since it is a less-polluted energy source compared with the conventional diesel fuel that is relatively more polluted. Biodiesel is prepared through a catalytic reaction of triglycerides and alcohol (usually methanol), in presence of catalyst. With the use of methanol, biodiesel produced is known as FAME. Biodiesel can be used in its pure form (B100). However, older vehicles may need minor modifications to the fuel lines and related rubber components to use it in its neat form. Pure biodiesel (B100) requires biodiesel compatible engine components. Currently B20

(20 % biodiesel and 80 % petroleum diesel, by volume) is the preferred choice, as the use of such ratio requires no engine modifications and no cold-weather complications were found. In UK and US, B20 is the blending choice. B20, the most commonly used form of biodiesel in the US, reduces net CO_2 emissions by 15.66 % per gallon of fuel used as studied by Sheehan et al. (1998). This has reduced the greenhouse gases (GHG) emission. However, bio portion in France increases (50 %, known as B50) in the vehicle fuel (World Energy Council, 2009). Biodiesel can also be used as an additive because it is a very effective lubricant enhancer (Ball et al., 1999).

2.1.1 Historical Background of Biodiesel Production

Diesel engine has become the engine of choice for power, reliability, and high fuel economy, worldwide as developed by Rudolph Diesel in the 1890s. Early experimenters on vegetable oil fuels included the French government and Dr. Diesel himself, who envisioned that pure vegetable oils could power early diesel engines for agriculture in remote areas of the world, where petroleum was not available at that moment. Modern biodiesel fuel, which is made by converting vegetable oils into compounds called fatty acid methyl esters (FAME), has its roots in research conducted in the 1930s in Belgium, but today's biodiesel industry was not established in Europe until the late 1980s.

Due to its clean emissions profile, ease of use, and many other benefits, biodiesel is quickly becoming one of the fastest growing alternative fuels in the world. Biodiesel future lies in the world's ability to produce renewable feedstock such as vegetable oils and fats to keep the biodiesel cost competitive with petroleum, without destroying natural ecosystems in the process or supplanting necessary land for food production. Creating biodiesel in a sustainable manner will allow this renewable, clean and cost effective fuel to help ease the world through shortages of petroleum, meanwhile encouraging economic and environmental benefits well into the 21st century.

2.1.2 Global Biodiesel Production

The annual increase of biodiesel production for past few years is shown in Table 2.1. In addition global biodiesel demand is predicted to grow by 15 %/year to 85 Mt by 2020. In the short term, at least 11 countries which are Germany, France, Italy, UK, Spain, Netherlands, US, Argentina, Brazil, Indonesia and Malaysia are expected to exceed a production of 1 Mt/year.

Table 2.1

Predicted annual increases in biodiesel production (Mt)

Producer	2008-2010	2011-2015
EU	1.7	1.2
USA	0.8	0.4
Asia-Pasific	1.1	1.4
South America	1.1	1.1
World	5.0	4.7

Source: Gunstone (2007)

Nowadays, most biodiesel are formed from plants that can also be utilized for food production (e.g. mango, sugar cane, wheat, corn, sugar beet, palm oil, rape, soy, etc). Even though biodiesel gives a number of benefits to society, there is a global debate in recent years regarding the impacts of biodiesel towards food production and prices, land harvest, carbon stores in forests and related issues.

A wide diversity of non-edible feedstock are abundant globally for biodiesel production including energy crops (e.g. jatropha, neem, miscanthus and short rotation copice), wastes (e.g. waste oils, food processing wastes, etc), agricultural residues (straw, corn stover, etc), forestry residues and novel feedstock, such as algae. Current R & D on biodiesel are mainly focused on:

- developing cost-competitive advanced technologies to convert wastes into fuels (waste into wealth);
- producing advanced properties fuel that are compatible with existing engines and infrastructues (for air, long-distance freight, and shipping).

2.1.3 Biodiesel in United States (US)

The most common source of oil for biodiesel production in the United State is soybean oil. It provides much of the early support for biodiesel in US came from the American Soybean Association. However, the demand for fuel consumption could not satisfy by the vegetable oil crops.

The function of biodiesel is similar to diesel fuel, mainly used for transportation. Annual biodiesel production was 545 million gallons in 2009. However, biodiesel production fell to 315 million gallons in 2010 due to the expiration and reinstatement of federal tax credits and renewable fuels standards. It was then risen up in 2011 to 1100 million gallons as referred to Figure 2.1. Soybean oil was the largest biodiesel feedstock in 2011, at 4136 million pounds consumed. According to data released by the U.S. Energy Information Administration (EIA. 2014), the next three greatest biodiesel feedstocks during 2011 after soybean oil were canola oil (847 million pounds), yellow grease and other recycled feedstocks (665 million pounds), and white grease (533 million pounds).

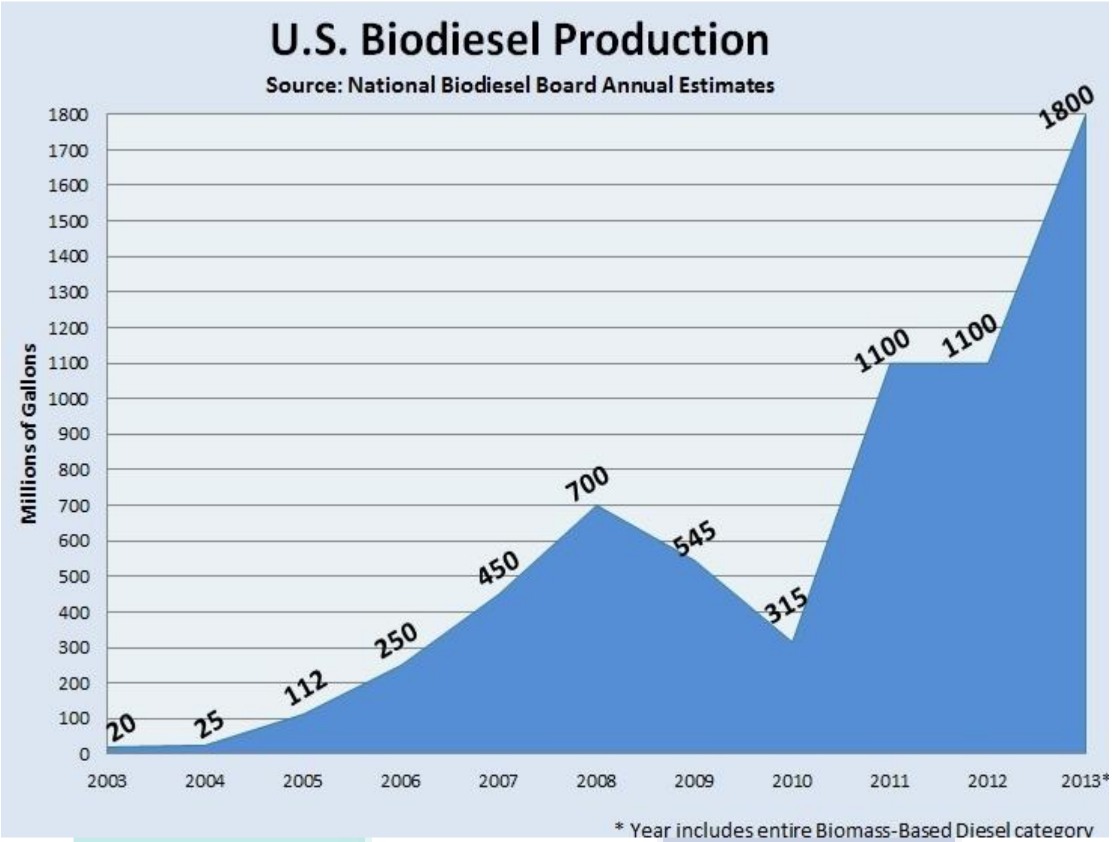


Figure 2.1 US biodiesel production.

Source: Bart et al. (2011)

President Obama supports the preservation of the Renewable Fuel Standard (RFS), as a part of energy strategy. However, there is fear that affordable private capital will unavailable to support any major capacity building for advanced biofuels; putting the RFS itself in considerable jeopardy, with its steep annual volumetric increases.

There has been considerable instability around RFS policy accordingly. In November, the EPA announced until 2015 that it was delaying finalization of the long-awaited 2014 Renewable Fuel Standard Renewable Volume Obligations. California has implemented a Low Carbon Fuel Standard (LCFS) in US. The standard is based on obligated parties meeting a targeted Carbon Intensity across all their fuels distribution in California, according to their preferred blend of alternative fuels, and the CI (carbon intensity) scores of those fuels. In order to reduce the carbon intensity of their products, LCFS need producers of petroleum-based fuels, beginning with 0.25 % in 2011 culminating in a 10 % total reduction in 2020. Petroleum importers, refiners and wholesalers can either develop their own low carbon fuel products or buy LCFS Credits from other companies that sell low carbon alternative fuels, such as natural gas biofuels, hydrogen or electricity.

Another state mandate worth noting is Minnesota's B10 biodiesel mandate. The departments stated that the four conditions required to move to B10 have been met. The policy was meant to come into place in 2012 with B20 planned for 2015. Those conditions were:

- federal standards for blend specifications
- the production capacity of biodiesel in Minnesota
- the amount of infrastructure and regulatory protocol for biodiesel blending
- the source of feedstocks.

The delaying in implementing B10 has also delayed the implementation of B20 in Minnesota. B20 was planned for 2015, but B10 will only now be implemented in July this year. Hence, Rep. Clark Johnson has proposed a bill that would delay B20 until 2018, giving three extra years to get blending facilities and gas stations ready to offer the fuel.

2.1.4 Biodiesel in Europe (EU)

Biodiesel has been produced on an industrial scale in the European Union since 1992, largely in response to positive signals from the EU institutions. Biodiesel is the most important biofuel in the EU, on volume basis, represents about 70 % of the total transport biofuels market, it is due is main European solution to reduce emissions from transport. Today, there are approximately 120 plants in the EU producing up to 6,100,000 tonnes of biodiesel annually. These plants are mainly located in Germany, Italy, Austria, France and Sweden (European Biodiesel Board, 2016).

Figure 2.2 showing the overall EU production decreased in 2012, reaching 9.6 million tonnes. This represents a 10 % decline compared to 2011. In 2009, biodiesel be the major contributor when the European Commission defined a 10 % use of renewable in the transport sector. Hence, decrease in European production is balanced by higher uncompetitive imports. Argentine and Indonesian biodiesel imports took over imports originating from the USA. The European Commissions imposed imports duties against subsidised US biodiesel in 2009.

Specific legislation is made to promote and regulate the use of biodiesel is in force in various countries including Austria, France, Germany, Italy and Sweden. The EU has also published strict guidelines in compliance with CEN Standardization (EN14214) in order to ensure quality and performance.

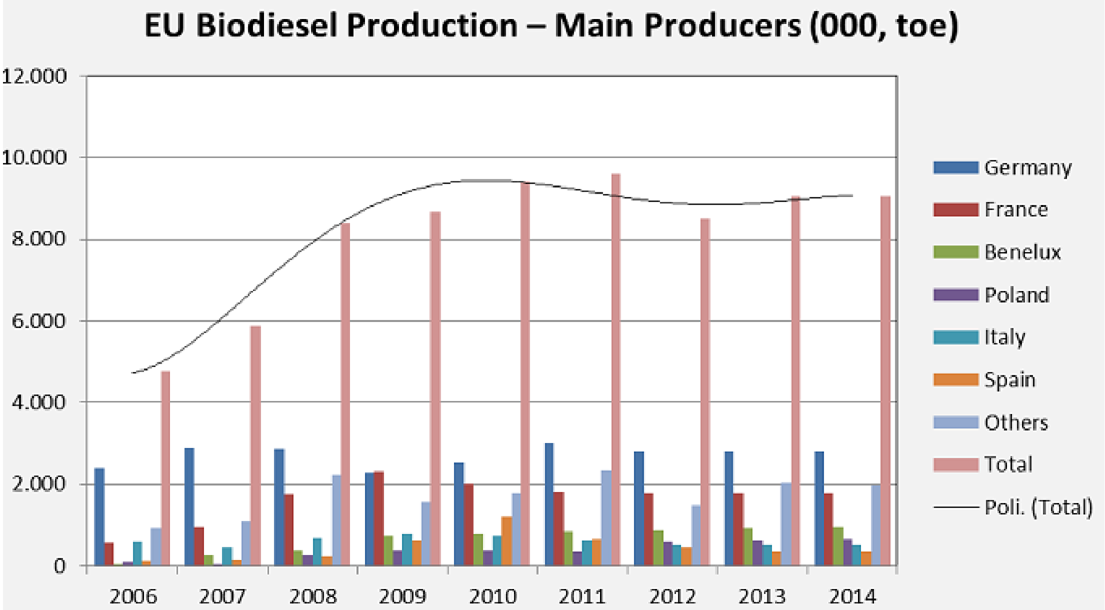


Figure 2.2 Biodiesel production in EU.

Source: Smith et al. (2013)

a) *Mandatory Requirement in Europe to use Biodiesel*

Due to the relatively low price of crude oil recently, biofuels are not competitive with the fossil fuel. Under the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) most industrialised countries have committed themselves to lower their greenhouse gases emissions (CO_2, HFCs, N_2O, CH_4, PFCs, SF_6) by 5.2 %. EU outlined the Biofuels Directive (EU Directive 2003/30/EC) on the promotion and use of biofuels and other renewable fuels for transport in May 2003. The general EU policy aims considered most relevant to the design of energy policy are:

(i) environmental protection
(ii) the competitiveness of the EU economy
(iii) the security of energy supplies.

EU has a 5.75 % mandate directive in place currently and was scheduled to move to 10 % by 2020. But in September 2013, the European Parliament voted to cap first generation ethanol consumption at 6 % of fuel demand by 2020 rather than the 10 % originally mandated by the Renewable Energy Directive. The vote passed with 356 votes in favor, 327 against and 14 abstentions. Tripartite negotiations with the Council of 28 member states and the European Commission are taking place later in the year to achieve a final rule.

Italian government's decision in October giving the biggest mandate news of the year worldwide to create a 0.6 % advanced biofuels blending mandate by 2018, the first in Europe to set up such a policy to boost demand for next generation fuels. Expected by 2022, that figure will increase up to 1 %. Beta Renewables produces 75 million liters per year at its facility in Crescentino and the country expects three more cellulosic ethanol plants to come online in southern Italy during the next year.

Recently, France's national oil body UFIP has agreed to increase the biodiesel blending mandate to 8 % from the current 7 %, with the official publication expected before the year's end. However it warned that going above 7 % may void some car manufacture warranties by going above the EU-wide approved 7 % level.

In UK, biofuel use in transport reached 4 % of the fuel supply during the second quarter of 2014, but ethanol has reached 4.5 % in the past. Ethanol blending is capped at 4.75 %. The Renewable Energy Association is strongly pushing for E10 blends to help the country achieve the 10 % biofuel mandate set by the EU for 2020.

2.1.5 Biodiesel in Asia

The business of biodiesel in Indonesia is expected to grow because the government intends to boost the biofuel program as detailed in the National Energy Policy, 2006. Nowadays, PERTAMINA increased to B10 (90 % petro-diesel blended with 10 % biodiesel) and selling Biosolar in East Indonesia (Sunardi, 2013).

Philippines mandated 2 % biodiesel blend (B2) in all diesels since February 6, 2009. Malaysia is one of the major global producers of palm oil which is 42.3 % of the world (Zhou and Thomson, 2009). It produced nearly 19 million tonnes of crude palm oil in year 2013 (MPOB, 2014). As such, Malaysia has very high potential for biofuel as it gives advantages from vast agricultural land and a tropical climate, in which oil palm plantations are very feasible.

Due to encourage the use of biofuels, Ministry of Plantation Industries and Commodities (MPIC) established the National Biofuel Policy (NBP) in line with the nation’s Five-Fuel Diversification Policy on 21 March 2006 (Ministry of Plantation Industries and Commodities, 2010). The National Biofuel Policy sets out to attain the following five objectives:

- supplementing the fossil fuels depletion with renewable resources
- mobilising local resources for biofuels
- exploiting local technology to provide energy for the industrial sectors and transportation
- paving the way for biofuels exporting
- benefiting from the spin-off effect of more stable palm oil prices

In Malaysia, the biodiesel initiatives started in 2006, 12 biodiesel plants are operated, with a total annual production capacity of 1.22 million tonnes from January to September in 2013 (Adnan, 2013). In June 2011, B5 biodiesel can be found in the market, the B5 biodiesel is an addition of 5 % biodiesel and 95 % of regular petroleum-based diesel which is suitable for the normal diesel engine vehicle without any modifications. According to The Star Online (2014) the biofuel option is seen as a safe net project for the palm oil sector, as when the price of crude palm oil (CPO) is about to drop and the palm oil stockpile about above the critical two million tonnes mark. (Rittgers and Wahab, 2013).

2.2 Biodiesel Production Method

Among the available biodiesel production technologies; transesterification, direct use and blending, micro-emulsification and pyrolysis; transesterification seems to be the best choice, as the physical characteristics of fatty acid esters are very close to those of diesel fuel and the process is relatively simple process compared to the others. The advantages and disadvantages of different methods in biodiesel production are presented in Table 2.2. There are four types of methods which is transesterification, direct use and blending, pyrolysis (thermal cracking) and micro-emulsions. Among these four methods, transesterification is the most chosen one because it provides lower emissions, renewability, higher combustion efficiency and higher cetane number.

Table 2.2

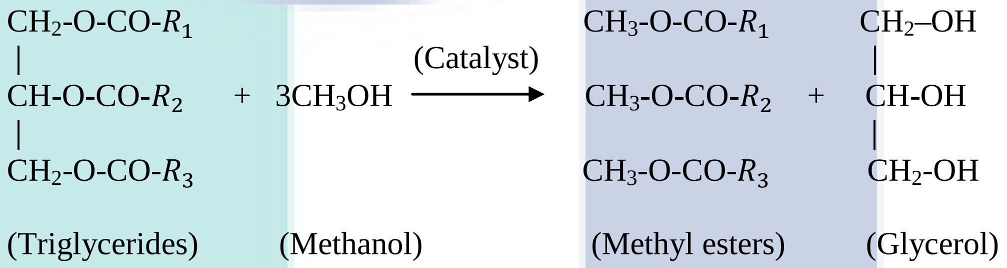
Method for biodiesel production

Methods	Definition	Advantages	Disadvantages
Transesterification	The reaction of a fat or oil with an alcohol in presence of catalyst forming esters and glycerol	Lower emissions; renewability; higher combustion efficiency; higher cetane number	Disposal of glycerol and waste water
Direct use and blending	Direct use as diesel fuel or blend with diesel fuel	Readily available; renewability Liquid nature-portability Heat content (~ 80 % of diesel fuel)	Higher volatility Higher viscosity The reactivity of unsaturated hydrocarbon chains
Pyrolysis (thermal cracking)	The conversion of long-chain and saturated substance to biodiesel by means of heat	The final product are similar to diesel fuel in composition	Intensive energy usage and greater cost
Micro-emulsions	A colloidal equilibrium dispersion of optically isotropic fluid microstructures with dimensions generally in the 1-150 nm range formed spontaneously from two immiscible liquids and one or more ionic or non-ionic amphiphiles	Better spray patterns during combustion Lower fuel viscosity	Lower cetane number Lower energy content

Source: Leung et al. (2010)

2.2.1 Transesterification Process

Transesterification is the conversion of a carboxylic acid ester into a different carboxylic acid ester. The most common method of transesterification is the reaction of the ester with an alcohol (e.g. methanol, ethanol) in the presence of catalyst. Methanol is preferred for its low cost, being the shortest alcohol chain and for its polarity (Demirbas et al., 2009). Although three moles of methanol are required, stoichiometrically, since transesterification is a reversible process, excess methanol is proposed to shift the reaction forward. Transesterification between triglyceride and alcohol is commonly known as alcoholysis, and, if methanol is used, then it is called methanolysis. The methanolysis of oil, together with a suitable catalyst, produces fatty acid methyl esters and glycerol. At the end of the reaction, the latter settles down to form the bottom layer. It is important to note that the main purpose of transesterification is to lower the viscosity and at the same time to increase the volatility of the oil. The overall transesterification process is normally a sequence of three consecutive steps, which is reversible reaction. The chemical reaction is shown in Figure 2.3.



$$\begin{array}{l} CH_2\text{-O-CO-}R_1 \\ | \\ CH\text{-O-CO-}R_2 \\ | \\ CH_2\text{-O-CO-}R_3 \end{array} + 3CH_3OH \xrightarrow{\text{(Catalyst)}} \begin{array}{l} CH_3\text{-O-CO-}R_1 \\ \\ CH_3\text{-O-CO-}R_2 \\ \\ CH_3\text{-O-CO-}R_3 \end{array} + \begin{array}{l} CH_2\text{–OH} \\ | \\ CH\text{-OH} \\ | \\ CH_2\text{-OH} \end{array}$$

Figure 2.3 Chemical reaction for transesterification process

Source: Leung et al., (2010)

Transesterification process can be carried out using homogeneous and heterogeneous catalyst. However, utilization of homogeneous catalysts such as KOH, CaO and NaOH give some drawbacks thus, a new process using heterogeneous catalyst has been developed for environment-friendly and reduction of production cost. Many types of heterogeneous catalysts from waste, such as waste egg, crab, and oyster shells; bone and ash (Boey et al., 2009; Nakatani et al., 2009; Chakraborty et al., 2010; Boey et al., 2011b, and Obadiah et al., 2012). *Paphia undulata* is second most important bivalve in Malaysia in term of total production and as a source of CaO.

a) Mechanical/Magnetic Assisted Transesterification

The transesterification of feedstock into biodiesel using waste catalyst was carried out in a 50 ml one-neck round bottom flask equipped with reflux condenser, thermometer, and magnetic heating mantle. In a typical reaction, feedstock oil was added in round bottom flask onto mixture of catalyst and methanol. The transesterification experiments were carried out at temperature 65 ± 2 ℃ and stirred vigorously. Reaction parameter include catalyst amount, methanol to oil molar ratio and reaction time were varied to identify the best conditions.

The resultant mixture was then cooled to room temperature. Successful transesterification reaction produced two liquid phases: methyl ester and crude glycerine, the heavier crude glycerine was settled at the bottom (Onukwuli et al., 2017).

b) *Ultrasonic Assisted Transesterification*

Biodiesel is normally produced in batch reactors that use heat and mechanical stirring (conventional method). Ultrasonic irradiation is a useful tool for emulsification of immiscible liquids. The low frequency ultrasound is an efficient, time saving and economically functional, offering a lot of advantages over the mechanical stirring. Ultrasounds can be a valuable tool for the transesterification of triglycerides to prepare the biodiesel at industrial scale.

Stavarache et al. (2005) stated that ultrasonic transesterifcation could achieve biodiesel yield of 99 %. In industry, ultrasonic can reduce the separation time from 5 to 10 h using mechanical stirring agitation, to less than 60 minutes. This method also helps in decreasing the amount of catalyst required by up to 50 %.

By using ultrasounds the reaction time is much shorter (10 - 40 min) than for mechanical stirring. The quantity of required catalyst is 2 or 3 times lower. The molar ratio of alcohol:oil used is only 6:1. Moreover, 40 kHz ultrasounds are effective in the reduction of the reaction time (10 - 20 min) meanwhile higher frequencies are not useful at all for the transesterification of fatty acids (Stavarache et al., 2005, and Gude and Grant, 2013)

c) *In situ Transesterification*

The method of *in situ* transesterification was considered of oil-containing in material directly contacts with catalyst alcohol and co-solvent in the reaction. It skips the extraction step and the oil-bearing material is put into contact with alcohol and in other words, the extraction and transesterification process take place simultaneously in the same equipment. Harrington and D'Arcy-Evans, (1985) claimed that *in situ* transesterification of sunflower seed produced higher methyl ester than mechanical stirring method and both processes yielded similar quality of fatty acid esters.

In situ transesterification is an alternative method of producing ME and has many advantages such us reduce the solvent used, production time and wastewater generation thus significantly maximizing the methyl ester yield (Leung et al., 2010). Suganya et al. (2014) found out that *in situ* transesterification of Enteromorpha compressa algal biomass produced 98.89 % of ME.

2.3 Waste Sources of Feedstock to Biodiesel Production

Obstacle for the utilization of biodiesel is that the high of biodiesel production cost, which is 1.5 to 3 times higher than that of petroleum diesel (Zhang et al., 2003; Haas et al., 2006, and Liu et al., 2012). Next, the question of food starvation arises when the trend indicates the need for large amounts of vegetable oil supply and if the major portion of the oil comes from neat edible oil. The concern in respect of food starvation or food for fuel already constitutes an argument. As globally there are 925 million people undernourished; stated by the Food and Agriculture Organization of the United Nations in 2011. In addition, with the increasing need for oil in the near future, it will definitely complicate the situation. Hence, the exploitation of raw materials waste source has been of recent interest. Researchers have effectively utilized chicken fat, beef tallow, waste cooking oil (WCO), spent bleaching clay (SBC), palm fatty acid distillate (PFAD), and decanter cake (DC) as a source of feedstock biodiesel (Ma et al., 1999; Chin et al., 2009; Lim et al., 2009; Malvade and Satpute, 2013, and Shi et al., 2013). Figure 2.4 shows the current and future global biodiesel production by feedstock.

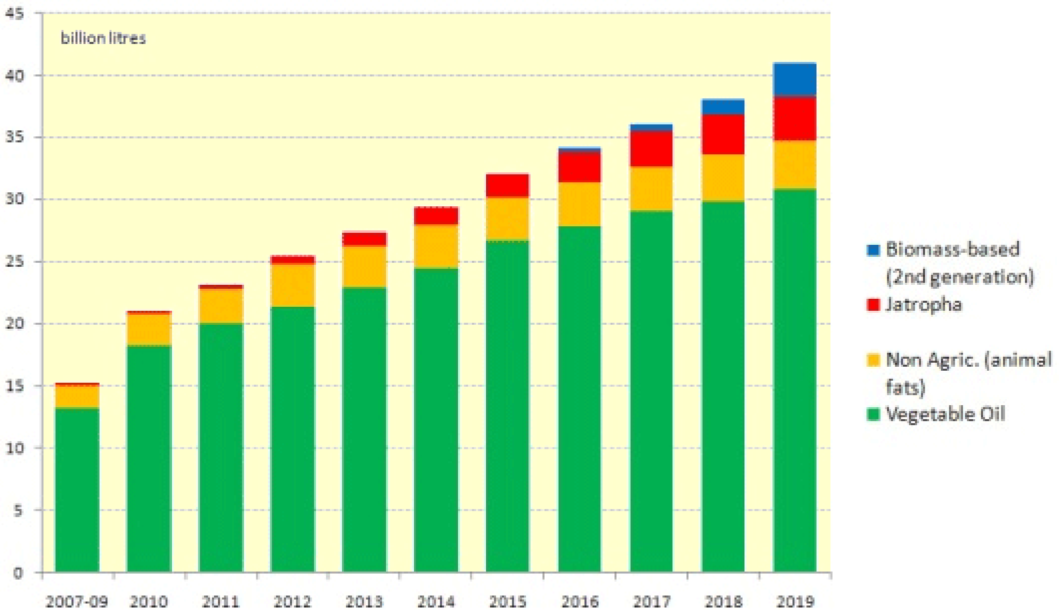


Figure 2.4 Global biodiesel production by feedstock.
Source: Shi et al. (2013)

Apparently, biodiesel seems to be costly than petro-diesel, which is more due to the high cost of the feedstock. The feedstock is the biggest input when making biodiesel. Few types of feedstock from edible and non-edible oil which are very common in the biodiesel industries such as soybean oil, *Jatropha* oil, palm oil, sunflower oil, rapeseed oil, canola oil, mango oil and neem oil. In addition, the concern of food starvation arises if edible oil is used. Next, limited supply and deforestation issue arises for non-edible feedstock. The utilization of oil from waste sources could also counter the environmental issue. The exploitation of waste materials has become very attractive reasoning to their abundance and low cost (Leung et al., 2010). For a solution, waste oil could be one of the best choices to produce biodiesel with a comparable cost to petro-diesel. Many studies have investigated the use of waste cooking oil (WCO); animal fats including chicken fats, lard, pork, tallow and grease, decanter cake (DC), spent bleaching clay (SBC) and palm fatty acid distillate (PFAD).

2.3.1 Spent Bleaching Clay

Waste from palm oil refinery which is spent bleaching clay (SBC), can be an affordable feedstock similar to waste cooking oil, animal fats and grease. Bleaching clay is used to remove soap, polymers, metals and colouring substances in the palm oil refinery. SBC contains high amount of oil, approximately 20 % - 40 % and the availability of SBC at refineries makes clay an attractive feedstock material for biodiesel (Ong, 1983). About 600,000 metric tonnes or more SBC is used worldwide annually. In Malaysia alone, it is estimated that about 200,000 tonnes of SBC is generated with a CPO production of 19.2 million tonnes in 2013 (MPOB, 2014).

The researchers compared two different catalysts to synthesize biodiesel from SBC oil. Sodium hydroxide and sulphuric acid were used as catalysts, and hexane was used to extract the oil from the SBC. Biodiesel yield was higher using an alkali catalyst compared to the acid catalyst. Moreover, reaction time using the alkali catalyst is much shorter as Hajjari et al. (2017) transesterification reaction produces 89.7 % methyl ester yield by utilized 3 wt.% KI with 10:1 methanol to oil molar ratio for 4 h reaction duration. *In situ* biodiesel production from residual oil from SBC was investigated by Mat et al. (2011). In other related study, the transesterification of SBC using different solvents was explored (Lim et al., 2009). The authors used different polar and non-polar solvents, such as methanol, ethanol, petroleum ether and hexane to convert the adsorbed oil on SBC to methyl ester. Among them, ethanol gave the highest extracts, which contains polar components and triglyceride. However, triglyceride without other components is preferred to fulfil the purpose of transesterification. As such, the non-polar solvent, provides the best extraction solvent, which extracts triglyceride (without polar components) from SBC with most least FFA content.

2.3.2 Animal Fats and Grease

The abundant availability of animal fats and the ease of collecting them from slaughter houses or meat processing units make it become one of the desired choices for biodiesel production feedstock. Animal fats and grease could be a suitably affordable feedstock for biodiesel synthesis (Demirbas, 2009).

However, there is a major disadvantage of animal fats and grease is that they provide products with poorer cold temperature properties than virgin vegetable oil and contain high FFA (Wyatt et al., 2005). Improving the cold properties of biodiesel using white sesame oil was investigated in which the researcher used methyl stearate, isopropyl stearate, methyl oleate and isopropyl oleate as pour point depressants

(Satapimonphan and Pengprecha, 2012). Another study was conducted by Wang et al. (2011) to improve the cold flow properties by using surfactants and detergent fractionation. The effect of different surfactants was studied, including sugar esters, silicone oil, polyglycerol ester, and diesel conditioner. In addition, blending biodiesel of poor cold properties with biodiesel with higher cold properties or using cold point depressants is such a method to recover cold properties (Kleinová et al., 2007).

The feedstock can be treated via esterification regarding the case of high FFA to reduce the FFA content. Researchers carried out esterification as a pretreatment step to convert the FFA to ester in order to deal with the high FFA in feedstock. In a related study, esterification was carried out using acids to esterify chicken fat with high FFA which is 13.45 %. After pretreatment, the FFA level in the feedstock was reduced to less than 1 % and methyl ester yield was 88.9 % (Chuah et al., 2017). The authors reported that sulphuric acid gave the best result in the following conditions: 20 % sulphuric acid, methanol to oil molar ratio 40:1 at 60 ℃ for an 80 min reaction. On the other hand, sulphamic acid did not have any significant effect in reducing the FFA (Alptekin and Canakci, 2010).

2.3.3 Decanter Cake

Solid wastes produce when the crude palm oil is centrifuged for purification where the supernatant is the pure palm oil and the sediment is the decanter cake (DC). DC does contain moisture (about 76 %, on wet basis), residual oil (about 12 %, on dry basis) and nutrients (about 6 %). There are previous reports on the use of DC in the area of bio-fertilizer, biofuel and cellulose (Kandiah, 2012, and Razak et al., 2012). Oil adsorbed on DC is a minor by-product of palm oil purification process with appreciable magnitude that could be a potential feedstock for production of biodiesel (methyl ester).

A large range of industrial wastes, both natural and synthetic, are disposed without extracting the useful components from them. Biomass is a promising source of renewable energy that contributes to energy needs and is the best alternative for guaranteeing energy for the future. Malaysia is the world’s second largest producer of palm oil and contributes 39% of the world’s total palm oil production (GGS, 2013). The total produced 19.22 million metric tonnes in 2013, with total 5.04 million hectares of land that are planted with oil palm trees (GGS, 2013, and MPOB, 2014), has an estimated total amount of processed fresh fruit bunches (FFB) of 7.8 tonnes/ha, 70% of which is removed as waste, such as palm press fiber (30%), empty fruit bunches (EFB, 28.5%), palm kernel shell (6%), decanter cake (DC, 3%) and others (2.5%) (Ramli et al., 2012, and Zafar, 2013). As such, in the processing of 39 million tonnes of FFB annually (7.8 tonnes/ha x 5 million ha), 1.17 million tonnes of waste DC (3% of 39 million tonnes FFB) is generated in Malaysia alone. Esterification of decanter cake produces 93.3 % of methyl ester yield (Maniam et al., 2013).

2.3.4 Waste Cooking Oil

Any vegetable oil that has been previously used for frying or cooking and which is deemed unhealthy to reuse is called as waste cooking oil (WCO) (See et al., 2006). Hence, one of the ways to add value to WCO is by utilizing it as a feedstock in transesterification. Table 2.3 depicts that WCO is one of the cheapest feedstock as it can be at ease collecting from households, hotels and restaurants. The price of these waste oils is two to three times cheaper than virgin vegetable oils (Demirbas, 2009).

The utilization of waste/used edible oils as raw material is a relevant idea, and there are many advantages for using waste feedstock for biodiesel production, namely:

- abundant supply
- relatively inexpensive
- environmental benefits

Waste oil in many countries is abundant (Tashtoush et al., 2004; Boey et al., 2011c; Wang et al., 2011, and Nurfitri et al., 2013). It was reported that, annually, EU recorded 0.7 - 1.0 million tonnes of waste oil, Turkey 350,000 tonnes and Canada 120,000 tonnes, in addition to those uncollected oils, which goes to waste through sinks and garbage and eventually seeps into the soil and water sources (Balkanlioğlu, 2012). In addition, it is realistically accepted that reusing used cooking oil for human consumption is harmful to health (See et al., 2006). According to Chen et al., 92.5% of methyl ester yield could be produced by using K_2CO_3 as a catalyst in transesterification of waste cooking oil at 12:1 methanol to oil molar ratio for 3 h (2017).

Table 2.3
Average international price of virgin vegetable oils, waste grease and fat in 2007

Feedstock	Price (US$/tonnes)
Rapeseed oil	824
Crude corn oil	802
Refined cottonseed oil	782
Soybean oil	771
Crude palm oil	543
Crude tea seed oil	514
Yellow grease	374
Poultry fat	256
Waste cooking oil	224

Source: Demirbas, (2009)

2.4 Extraction Techniques

Nowadays, there are many techniques to extract oil. Every of this technique has its own benefit and drawback, depending on what is the material being extracted. Among the most popular techniques had been used in many extraction activities are electromechanic, enzymatic, expeller, osmotic and supercritical. The solvent extraction method and ultrasonic is found out to be cheaper and easier for conducting residual oil.

Soxhlet extraction is the technique of removing one constituent from a solid by means of a liquid solvent or called as leaching. Soxhlet extraction has been investigated for a long time as a feedstock extraction method for biodiesel production, especially in non-edible oil such as Jatropha seed, *Pmgamia pinnata*, *Coriandrum sativum* L., *Cerbera odollam* (Sea mango) and *Moringa oleifera* (Achten et al., 2008; Mahanta and Shrivastava, 2008; Kansedo et al., 2009b, and Sarin et al., 2009).

Mahanta and Shrivastava (2008) and Achten et al. (2008) reported that Soxhlet extraction with n-hexane can be used to extract the oil from *Jatropha* seed and *Pmgamia pinnata*. This method could produce about 41 % and 95 - 99 % of oil yield respectively. Few other studies conducted by Kansedo et al. (2009a) and Sarin et al.

(2009), extracted the oil from *Cerbera odollam* (sea mango), Coriander (*Coriandrum sativum L.*), *Moringa oleifera* and *Guizotia abyssinica L.* using Soxhlet extractor with n-hexane as the solvent.

Frequently used solvent are *n*-hexane, petroleum ether, ethanol and benzene. Due to its smaller polarity level as a solvent and relatively cheaper cost, *n*-hexane is chosen apart from easy to get. Several things need to be considered in choosing solvent are polarity level, toxicity level, volality and the price. Ethanol is chosen because it has longer carbon than methanol and the longer the carbon chains the smaller is the polarity level. By such, it will be easier to extract the oil.

Ultrasonic assisted extraction method is a new extraction method, alternative to mechanical stirring extraction technique. This method is indicated to be inexpensive, simplicity, shorter extraction time and less-energy usage. The use of ultrasonic cause the cavitation bubbles in solution, acoustic cavitation phenomenon which created by passing ultrasound waves through solvent system causing higher efficiency of the technique (Chuah et al., 2017). This phenomenon increases the release of the solutes from the matrix to the solvent by permitting better penetration of the solvent into the sample (Morelli and Prado, 2012).

Yustianingsih et al. (2009) extracted oil from rice bran to produce biodiesel. Furthermore, Zhang et al. (2003) compared both ultrasonic-assisted and mechanical stirring methods for oil extraction from flaxseed and concluded that ultrasound is more efficient than the mechanical stirring method for oil extraction. In addition, it concluded that the ultrasound-assisted technique gave highest oil yield of 93.3% after being compared with other technique (Luthria et al., 2007).

2.5 Catalysts in Transesterification

2.5.1 Homogeneous Catalyst

Transesterification of triglycerides catalyzed by homogeneous base catalyst is common process in the industrial biodiesel production. It has many advantages which are very fast reaction rate about 4000 times faster than acid-catalyzed transesterification. In addition, reaction can occur at mild reaction condition and less energy intensive. Meanwhile, catalysts such as NaOH and KOH are relatively cheap, widely available and could produce more than 95% methyl ester yield. But, this catalyst is sensitive to FFA content in the oil, soap will form if the FFA content in the oil is more than 2 wt.% thus too much soap formation will decrease the biodiesel yield and cause problem during product purification especially generating huge amount of wastewater (Wang et al., 2006). A list of homogeneous catalyst is presented in Table 2.4.

Table 2.4

Transesterification reaction catalyzed by homogeneous catalysts

Catalysts	**References**
	Homogeneous base catalysts
Potassium hydroxide	Singh et al., 2006, and Vicente et al., 2004
Sodium hydroxide	Singh et al., 2006; Ma and Hanna, 1999, and Vicente et al., 2004
Potassium methoxides	Singh et al., 2006, and Vicente et al., 2004
Sodium methoxides	Freedman et al., 1986; Singh et al., 2006; Ma and Hanna, 1999, and Vicente et al., 2004
	Homogeneous acid catalysts
Sulphuric acid	Freedman et al., 1986
Hydrochloric acid	Ayhan, 2008

For homogeneous acid catalysed reaction, it is insensitive to FFA and water content in the oil, being preferred-method if low-grade oil is used (PFAD, DC, etc.). Furthermore, esterification and transesterification occur simultaneously. Reaction can occur at mild reaction condition and less energy intensive but it precedes a very slow reaction rate. On the other hand, corrosive catalyst such as H_2SO_4 used can lead to corrosion on reactor and pipelines if applied to industrial scale. Separation of catalyst from product is also problematic as investigated by Singh et al., (2006) and Arzamendi et al., (2008).

2.5.2 Heterogeneous Catalyst

Similar to homogeneous catalyst, heterogeneous catalyst also can be classified into acid and base categories. There are some advantages of heterogeneous base catalyst such as faster reaction rate (able to achieve more than 90% methyl ester yield in 1 h reaction) than acid-catalyzed transesterification, moreover reaction can occur at mild reaction condition and thus less energy intensive, easy separation of catalyst from product, high possibility to reuse and regenerate the catalyst. Meanwhile few drawbacks of heterogeneous base catalysts are catalyst poisoning when exposed to ambient air, sensitive to FFA content in the oil due to its basicity property, soap formation when FFA content in the oil is more than 2 wt.% which may decrease the biodiesel yield and cause problem during product purification and last but not least, leaching of catalyst active sites may affect the product as stated by Kouzu et al. (2008).

While for heterogeneous acid catalyst, it is insensitive to FFA and water content in the oil and being one of the preferred-method if low-grade oil is used. In addition, esterification and transesterification can occur simultaneously. It is also energy intensive and provides ease of separation. There is also high possibility to reuse and regenerate the catalyst. However, the disadvantages are as such complicated catalyst synthesis procedures lead to higher cost. Normally in order to utilize this type of catalyst, high reaction temperature, high alcohol to oil molar ratio and long reaction time are required and product might be contaminated if leaching of catalyst active sites occur (Miao and Gao, 1997). The list of various heterogeneous catalysts is presented in Table 2.5 below.

Table 2.5

Transesterification reaction catalyzed by heterogeneous catalysts

Catalysts	References
	Heterogeneous base catalysts
SrO	Liu et al., 2007
MgO	Demirbas, 2008
CaO	Kouzu et al., 2008
KF/CaO-MgO	Fan et al., 2012
	Heterogeneous acid catalysts
SO_4^{2+}/ZrO_2	Miao and Gao, 1997
SO_4^{2+}/SnO_2	Gutierrez-Baez et al., 2004
ZrO_2-Al_2O_3	Furuta et al., 2004

2.6 Catalysts from Different Types of Support Materials

A comprehensive summary on the metal loaded support material as catalyst is presented in Table 2.6. The utilization of oil and catalyst from waste sources could also counter the environmental crisis. Furthermore, within the last five years, many research works have focused on the exploitation of waste materials as catalysts for the production of biodiesel. Due to their high methyl ester conversion using metal loaded support material as a catalyst in transesterification reaction, this type of research work has become very attractive. There are many ways in preparing catalysts such as wet impregnation method, co-precipitation, sol-gel, physical adsorption mechanism, ion exchange, grafting, solid state method, microwave irradiation, hydrolysis, immobilized cross linking reaction and calcination. For catalyst performance, it is influenced by several factors such as basicity or acidity, surface area, pore volume, pore diameter, calcination temperature and duration, particle size, amount of metal loaded on support and porosity.

Table 2.6

Summary of various types of metal loaded support material as catalyst

Support	Metal	Metal loading	Feedstock	Method for catalyst preparation	Factor influence catalyst performance	Best condition				ME (%) C=Conversion Y=Yield	Reusability	Ref
						Temp. (°C)	Catalyst amount	Time (h)	MeOH to oil molar ratio			
Heterogeneous base												
Coal fly ash	CaO	30 wt%	Soybean	Wet impregnation, calcination 1000 °C, 2h	Basicity, surface area (0.7m^2/g), pore volume (0.0044cm^3/g) and pore diameter (5.2nm)	70	1.0 wt%	5	6.9:1	96.97 (Y)	16	Chakraborty et al., 2010
Palm oil mill fly ash	CaO	45 wt%	Crude palm	Wet impregnation, calcination 850 °C, 2h	Calcination temperature and duration, surface area (3.5m^2/g) and basicity	45	6.0 wt%	3	12:1	79.76 (C)	3	Ho et al., 2014
Fly ash	Calcined CaCO$_3$	15 wt%	Crude palm	Wet impregnation, calcination 900 °C, 5h	Porosity, basicity, CaCO$_3$ calcination temperature (800 °C), surface area of fly ash (1.7m^2/g)	60	2.0 wt%	3	12:1	94.48 (C)	-	Ho et al., 2012
Oyster shell	KI	1mmol/g	Soybean	Wet impregnation, calcination 300 °C, 2h	Surface area (6m^2/g)	50	1 g	4	10:1	≈85 (C)	3	Jairam et al., 2012
Al$_2$O$_3$	KOH	25 wt%	Palm	Wet impregnation, calcination 500 °C, 3h	Surface area (7.7 m^2/g)	60	3.0 wt%	2	15:1	91.07 (Y)	-	Noiroj et al., 2009

Table 2.6 continued.

	CaO-MgO (8:2, wt.)	12.5 wt%	Cottonseed	Co-precipitation, calcination 700 ℃, 5h	Basicity, particle size	95	0.1 g	3	8.5:1	92.45 (C)	4	Mahdavi et al., 2014
	KNO_3	35 wt%	Soybean	Wet impregnation, calcination 500 ℃, 5h	Basicity, calcination temperature and duration	MeOH refluxing temp.	6.5 wt%	7	15:1	87.0 (C)	-	Xie et al., 2006
	KI	35 wt%	Soybean	Wet impregnation, calcination 500 ℃, 3h	Calcination temperature and duration, basicity	MeOH refluxing temp.	2.5 wt%	8	15:1	96.0 (C)	-	Xie and Li, 2006
	KOH	15 wt%	Waste cooking	Wet impregnation, dried 100 ℃ overnight	Amount of metal loading, basic sites, calcination	70	5.0 wt%	2	9:1	96.8 (Y)	3	Agarwal et al., 2012
	CsF	20 wt%	Sunflower	Wet impregnation, dried 120 ℃, 12h	Catalyst activation temperature (450 ℃, 2h), basicity, basic sites	75	1.09% (wt/v)	1	4:1	>90 (C)	5	Verziu et al., 2009
γ-Al_2O_3	KF	0.24g KF/g γ-Al_2O_3	Palm	Sol-gel, wet impregnation, calcination 500 ℃, 3h	Basicity (basic sites), pore size and surface area (143m^2/g)	60	4.0 wt%	4	14:1	80.0(Y)	-	Islam et al., 2013
	$NaNO_3$	0.30g $NaNO_3$/g γ-Al_2O_3			Basicity (basic sites), pore size and surface area (152m^2/g)					87.7(Y)		
	NaOH	10.7 wt%	Sunflower	Wet impregnation, dried 120 ℃, 12h	Amount of metal loaded, calcination, basic sites, surface area (90m^2/g)	50	2.0 wt%	8.5	12:1	≈99.0 (C)	-	Arzamendi et al., 2007
	K_2CO_3	8.7 wt%	Sunflower	Wet impregnation, dried 120 ℃ overnight, activation 550 ℃, 2h	Basicity, activation temperature and duration	60	5.56 wt%	1	25:1	99.0 (C)	1st run= 99% (2nd=33, 3rd=6.5, 4th=3.8)	Alonso et al., 2007

Aluminosilicate layers	KOH	35 wt%	Soybean	Impregnation, physical adsorption mechanism, dried 120 ℃, 24h	Basic sites of $-O^{-}-K^{+}$	60	6.52 wt%	2.5	70:1	98.0 (C)	-	Rashtizadeh et al., 2010
Alumina silica	K_2CO_3	45 wt%	Sunflower	Sol-gel, calcination 600 ℃, 12h	Pore size, calcination temperature	120	2.0 wt%	2	15:1	97.7 (Y)	2	Lukic et al., 2009
Mesoporous silica (SBA-15)	CaO	14 wt%	Sunflower Castor	Wet impregnation, calcination 550 ℃, 6h	Basicity	60	1 wt%	5 1	12:1	95 (C) 65.7 (C)	-	Albuquerque et al., 2008
Meso-macroporous silica	CaO	50 wt%	Palm	Wet impregnation, 800 ℃, 4h	Pellet size (325 μm), basicity	60	5.0 wt%	6	12:1	94.15 (Y)	5	Witoon et al., 2014
AlSBA-15	K_2SiO_3	30 wt%	Jatropha	Wet impregnation, calcination 600 ℃, 2h	Calcination temperature, basicity, surface area (654.0 m^2/g), amount of metal loaded to support	60	3.0 wt%	1.5	9:1	95 (Y)	5	Wu et al., 2014
SBA15	Tetraalkylammonium hydroxide	1:1 g/g SBA15	Soybean	Grafting, ion exchange, stir magnetically, Soxhlet extraction, dried 70 ℃, 12h	Basicity, surface area	Methanol refluxing temp.	2.5 wt%	0.5	12:1	99.4 (Y)	5	Xie and Fan, 2014
	$CsNO_3$	2 wt wt%	Canola	Wet impregnation, calcination 500 ℃, 5h	Pore size, surface area (628.2m^2/g)	135 ℃ in pressurized reactor	7.69 mg/ml oil	5	40:1	25.35 (Y)	-	Kazemian et al., 2013
	Tetramethylguanidine	2.0 g	Soybean	Wet impregnation, dried 50 ℃, 12h	Basicity, surface area (325m^2/g), pore volume (0.5cm^3/g)	MeOH refluxing temp.	5.0 wt%	12	15:1	91.7 (C)	5	Xie and Fan, 2013
MCM-41	Mg-Al hydrotalcite	Mg:Al = 3:1	Soybean frying	Wet impregnation, calcination 500 ℃, 3h	Basicity, porosity	60	10 wt%	24 5	13ml MeOH /g oil	97.0 (C) mechanical stirring (600rpm) 96. 0 (C) ultrasonication (24kHz)	-	Georgogianni et al., 2009

NaX-zeolite	KNO_3	35 wt%	Sunflower	Wet impregnation,calcination 500 ℃, 4h	Basicity, number of basic sites	60	10.0 wt%	6	21:1	98.2 (Y)	- not sudied	Pena et al., 2013
	KOH	10 wt%	Palm	Wet impregnation, dried 110 ℃, 24h	Surface area (35.6 m^2/g)	60	6.0 wt%	3	15:1	91.07 (Y)	-	Noiroj et al., 2009
NaY zeolite	CaO	30 wt%	Soybean	Microwave irradiation, grinded, dried (600 ℃, 2h)	Surface area, basicity	65	3.0 wt %	3	9:1	95.0 (Y)	-	Wu et al., 2013
	Na	4 wt%	Triolein	Ion exchange (Na^+) 500 ℃, 8h	Duration of ion exchange process, basicity	65	1.0 wt%	1	15:1 (mass ratio)	97.3 (Y)	3	Wang et al., 2013
HY zeolite	K	20 wt%	Waste cooking oil	Wet impregnation, calcination 400 ℃, 3h	Basicity	65	7.0 wt%	3	14:1	93.2 (Y)	3	Chuah et al., 2017
Nd_2O_3	KOH	30 wt%	Soybean	Wet impregnation , calcination 600 ℃, 2h	Calcination temperature, basicity	60	6.0 wt%	1.5	14:1	92.41 (Y)	5	Li et al., 2011
Al-Ca hydrotalcite (1:3, molar)	K_2CO_3	25 wt%	Soybean	Solid-state mixing method, calcination 650 ℃, 5h	Calcination temperature, basic strength	65	2.0 wt%	2	13:1	95.1 (Y)	4	Sun et al., 2014
SrO	CuO	10 wt%	Hempseed	Precipitation, calcination in vacuum 1000 ℃, 5h	Basicity, surface area (2.5m^2/g), pore size (41.2nm), amount of metal loaded	180	3 wt%	3	12:1	92.0 (Y)	8	Su et al., 2013
Cinder	CaO/ KF	5g CaO, 10g KF in 10g cinder	Soybean	Wet impregnation, calcination 500 ℃, 5h	Basicity	65	2.1 wt%	0.33	12:1	99.9 (C)	4	Liu et al., 2012
TiO_2	$C_4H_4O_6HK$	0.7:1 (K:TiO_2)	*S. marianum*	24h wet impregnation, calcination 600 ℃, 6h	Calcination temperature and duration, basicity, amount of metal loaded and type of support	60	5.0 wt %	0.5	16:1	90.1 (Y)	5	Takase et al., 2014
ZrO_2	La_2O_3	21 wt%	Sunflower	Wet	Basicity,	200	5 wt %	5	30:1	84.9 (Y) 96.0	5	Sun et al.,

ZnO				impregnation, calcination 600 ℃, 4h	calcination temperature, amount of metal loaded to support					(C)		2010
	KOH	32 wt%	*S. marianum*	Wet impregnation, calcination 530 ℃, 5h	Basicity, amount of metal loaded	60	6 wt%	2	15:1	90.8 (Y)	5	Takase et al., 2014
	$Sr(NO_3)_2$	2.5mmol/g ZnO	Soybean	Wet impregnation, calcination 600 ℃, 5h	Basicity, calcination temperature	65	5.0 wt%	5	12:1	94.7 (C) 96.8 (C) with co-solvent	1 (15.4%)	Yang et al., 2007
	CaO	16 wt%	Sunflower	Wet impregnation, calcined 600 ℃, 6h	Calcination temperature, amount of metal loaded to support, activation temperature and duration, 800 ℃, 1h	60	1.3 wt%	2	12:1	>90 (Y)	-	Alba-Rubio et al., 2010
Heterogeneous Acid												
ZSM5 Zeolite	Modified strontium with barium (Ba-Sr)	6 wt% Sr based on support, 4 wt% Ba based on Sr wt.	Sunflower	Incipient wetness impregnation, calcined 600 ℃, 6h	Calcination temperature and duration, surface area (224.3 m^2/g)	60	3.0 wt%	3	9:1	87.7 (Y)	-	Feyzi and Khajavi, 2014
SnO_2	WO_3	30 wt%	Soybean	Wet impregnation, calcined 900 ℃, 5h	Calcination temperature (900 ℃), amount of metal loading	110	5.0 wt %	5	30:1	79.2 (C)	4	Xie and Wang, 2013
SBA-15	TSA_3	30 wt%	Waste cooking	Impregnation	Surface area (645m^2/g), acid sites	65	6.0 wt%	8	8:1	86.0 (C)	4	Narkhede et al., 2014
MCM-41	p-toluene sulfonic acid (PTSA)	15 mL PTSA/g support	Soybean	Immersing MCM-41 into 0.2 mol/L PTSA solution 24 h, dried 140 ℃ overnight	Circulation velocity, trans-membrane pressure 80kPa	80	0.27 g/cm^3	3	24:1	84.1 (Y)	3	Xu et al., 2014
$AlPO_4$	WO_3	30 wt%	Soybean	Precipitation, incipient impregnation,	Pore size, calcination temperature,	180	5 wt%	5	30:1	72.5 (C)	4	Xie and Yang, 2012

				calcined 800 ℃, 5h	amount of catalyst loading						
ZrO_2	Isopoly tungstates (WO_3)	15 wt%	Sunflower	Precipitation, calcined 750 ℃, 4h	Calcination temperature, amount of catalyst loading, surface area (102 m^2/g) , acidity	200	3.0 wt%	5	15:1	97.0 (C)	-	Sunita et al., 2008
	Chlorosulfonic acid ($HClSO_3$)	1g $Zr(OH)_4$ stir in 15ml 0.5M $HClSO_3$	Rice bran	Hydrolysis, calcined 600 ℃, 3h	Surface area (61m^2/g), acid sites	120	6.0 wt%	12	12:1	100.0 (Y)	3	Zhang et al., 2013
	Sr	14 wt% $SrNO_3$ (aq.) onto 15g ZrO_2	Waste cooking	Wet impregnation, calcined 650 ℃, 5h	Surface area, acid and basic sites balanced, amount of metal loaded	115.5	2.7 wt%	2.8	29:1	79.7 (Y)	-	Omar and Amin, 2011
Biocatalyst												
Modified attapulgite	*Bukholderia cepacia* lipase (Enzyme)	7 wt% water on 10 wt% lipase	Jathropha	Immobilized cross-linking reaction	Water	35	8.0 wt%	24	6.6:1	94 (Y)	15	You et al., 2013

Temp = Temperature, MeOH = Methanol

2.6.1 Fly ash

An inorganic waste generated from coal combustion processes is called as fly ash. It has a typical chemical composition (on dry basis), of around 55 % SiO_2, 30 % Al_2O_3 and other oxides (Ojha et al., 2005). Obviously, the oxides of both silica and alumina could work excellently as a catalyst support. Apparently, researchers have used thermally activated fly ash as a support for loading CaO for chemical production. This supported catalyst gave higher conversions of up to three cycles and the catalyst was able to be reused without much loss in the reaction. High amount of SiO_2 and Al_2O_3 prompts its potential applicability as a low-cost catalyst support. Fly ash supported CaO has been employed as a recyclable solid base catalyst in a recent work by Jain et al., (2010). Fly ash supported heterogeneous CaO catalyst from egg shells have been investigated to transesterify soybean oil (Chakraborty et al., 2010). Fly ash supported a CaO catalyst prepared by wet impregnation method, with 30 wt.% CaO loading and followed by calcination at 1000 ℃ for 2 h. With the reaction condition 6.9:1 MeOH:oil molar ratio, maximum FAME yield of 97 % was achieved. The study of the reusability of catalyst showed higher catalytic activity in which the catalyst showed remarkable repeated usability of 16 times without major loss in activity which means adapting the high stability of the catalyst. However, the catalyst became completely deactivated after being used more than 18 times. Fly ash-based base catalyst was conducted, in the transesterification reaction of sunflower oil by Kotwal et al. (2009). The catalyst was prepared by the mechanical stirring wet impregnation method using KNO_3. In that work, fly ash loaded with 5 wt.% KNO_3, followed by calcination at 500 ℃ was able to convert the oil at 87.5 % in 8 h reaction time. However, the catalyst unable to be reused, probably due to the leaching of active species. Similarly, Babajide et al. (2010), reported that fly ash loaded with 5 wt.% KNO_3 could transesterify sunflower oil to about 86% but at an elevated reaction temperature of 160 ℃. Similar to the previous study, the catalyst also suffers with respect to its reusability.

2.6.2 Alumina

Supported alkali metal hydroxides are among the most-investigated solid heterogeneous catalytic systems in transesterification reaction. Most authors reported on the K-based catalysts, particularly Al_2O_3-supported catalysts. This type of catalyst is attractive because of the high basicity and relatively cheap and easy process for transesterification (Kutalek et al., 2014). Several researchers have reported that solid K-based catalysts with higher catalytic activity; for example, esters yield higher than 90 % using K_2CO_3/Al_2O_3, KNO_3/Al_2O_3 and KF/Al_2O_3 under 15:1 methanol to oil molr ratio and 3 h reaction duration (Onukwuli et al., 2017). However, the main crisis in application of these catalysts is their stability.

At the laboratory scale, various heterogeneous catalysts have been developed which are tested in alcoholysis reaction. The catalysts used are either zinc oxide or a mixture of zinc oxide with alumina or a zinc aluminate. Alumina loaded with alkali metal salts or different potassium compound was demonstrated as an efficient solid-base catalyst for the alcoholysis of vegetable oils as reported by Noiroj et al., (2009). Alumina exhibits no activity but when loaded with KI, KF, KNO_3, KOH or K_2CO_3 and activated at high temperature, the supported catalyst showed catalytic activities.

2.6.3 Mesoporous Santa Barbara Amorphous-15 (SBA-15)

Development of appropriate heterogeneous acid catalysts is in need to manage major drawbacks such as longer reaction time, requirement of high reaction temperature and catalyst deactivation. Hence, one of the important classes of catalysts is organic-inorganic hybrid mesoporous materials prepared by anchoring various acidic functional groups on the inert support materials such as SBA-15 (Shah et al., 2014). Several researchers have demonstrated potential of organic acid functionalized mesoporous silicas in biodiesel manufacturing from various feedstocks such as beef tallow, crude vegetable oils and low grade oils.

Recently, Dacquin et al. (2012) reported that by enlarging the mesopores (>8 nm) of sulfonic acid functionalized SBA-15 catalysts result in rapid transport conduits to the active sites thus improving the catalytic performance in biodiesel synthesis.

2.6.4 Mobil Composition of Matter-41 (MCM-41)

P-toluenesulfonic (PTSA) is found to be an effective acid catalyst for esterification or transesterification reaction and MCM-41 presents significant advantages as a catalyst support due to its high specific surface areas, large pore sizes and high thermal stability (Xu et al., 2014). In addition, PTSA supported MCM-41 in transesterification of soybean oil produced 84.1 % biodiesel yield.

2.6.5 Zirconia

Heterogeneous catalysts are more preferable than homogeneous catalysts in the biodiesel production. Zirconia supported catalyst is claimed to be an interesting material since it has amphoteric nature along with redox properties which could be either acid or base catalyst if the catalyst was pre-treated well (Omar and Amin, 2011). TiO_2/ZrO_2 (11 wt.% Ti) was reported to produce biodiesel more than 99.5 %.

On the other hand, the basicity of zirconia can be enhanced by modifying it with alkali promoter such as potassium hydroxide, magnesium metal and lanthanum oxide. The activity of La_2O_3/ZrO_2 was tested through transesterification of sunflower oil at 200 ℃, with 1:30 ratio of oil:methanol and 5 wt.% catalyst loading for 5 h reaction duration. The catalyst with 21 wt.% of La_2O_3 doped on ZrO_2 gives the highest ME yield at 96 %. Meanwhile, Sheehan et al. (2009) reported that Mg/Zr is effective to sunflower oil transesterification and other non-edible oil.

2.7 Effect of Free Fatty Acid and Moisture to Transesterification

Two major impurities that affect the quality of oils are free fatty acid (FFA) and moisture content. For the transesterification used homogeneous catalyst, the reaction must be free of moisture (< 0.06% w/w) and FFA (< 0.5%) (Freedman et al., 1986; and Ma and Hanna, 1999). Wright et al. (1944) noted that the triglycerides should have an acid value less than 1, and material should be substantially anhydrous. Sodium hydroxide (NaOH) is required to neutralize the FFA if acid value greater than 1. The presence in the reaction can lead to saponification reaction, the soap formation reaction as shown in Figure 2.5.

$$\underset{\text{Fatty acid}}{RCOOH} \quad + \quad \underset{\text{Hydroxide}}{XOH} \quad \rightleftharpoons \quad \underset{\text{Soap}}{RCOO^{-}X^{+}} \quad + \quad \underset{\text{Water}}{H_2O} \quad (X = \text{Na or K})$$

Figure 2.5 Saponification reaction of fatty acid.

Unfortunately, the presence of moisture can lead to hydrolysis of the ester that produces fatty acids and methanol, as shown in the following reaction (Figure 2.6):

$$\underset{\text{Ester}}{RCOOCH_3} \quad + \quad \underset{\text{Water}}{H_2O} \quad \rightleftharpoons \quad \underset{\text{Fatty acid}}{RCOOH} \quad + \quad \underset{\text{Methanol}}{CH_3OH}$$

Figure 2.6 Hydrolysis reaction of ester.

To be precise, the presence of FFA or moisture, or both will lead to the soap formation reaction (saponification). The soap promotes the formation of stable emulsions, which lowering methyl esters yield and complicating downstream separation process of methyl esters and glycerol. Extra processing is required to remove the FFA regarding the lower yield, moisture and the soap resulting from the reaction mixture. In a previous report, an increase in FFA content from 5 to 33 % decreased the yield from 90 % to as low as 58 % (Canacki and Gerpen, 2001).

The heterogeneous catalysts showed better water tolerance than homogeneous catalysts, the presence of water in the reaction system could change the Lewis base site of metal –O– group into Bronsted base sites of metal –OH group (Yan et al., 2009).

CHAPTER 3

MATERIALS AND METHODS

3.1 Materials

Refined, bleached and deodorized palm olein (RBD-PO) was manufactured by Yee Lee Edible Oils Sdn. Bhd. (Shah Alam, Selangor) and purchased from a local grocery. Waste palm cooking oil (WPCO) was collected from cafeteria surrounding Universiti Malaysia Pahang (UMP). Spent bleaching clay (SBC) was collected from palm oil refinery, Felda Vegetable Oils Sdn. Bhd. in Kuantan Port. Analytical grade methanol and *n*-hexane were purchased from MERCK (Germany). Chloroform, phenolphtalein, petroleum ether (40 - 60 ℃) and Thin Layer Chromatography (TLC) (20 × 20 cm, silica gel 60 F254) of HPTLC grade were purchased from MERCK (Germany). The chemicals were purchased from Sigma-Aldrich company (Switzerland) include KOH, CaO, $LaCl_3$, Hammett indicators: phenolphthalein (H_= 8.2); 2,4-dinitroaniline (H_= 15.0) and 4-nitroaniline (H_= 18.4), methyl heptadecanoate as an internal standard GC grades (purity > 99.1 %). Methanol (anhydrous, ≥ 99.8 %) was purchased from Hamburg (Germany).

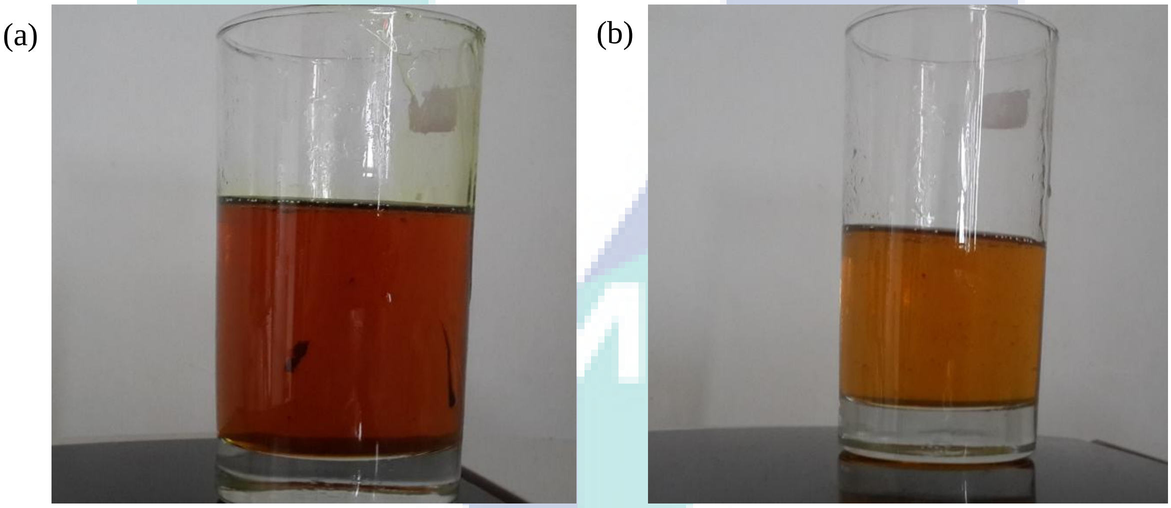
3.2 Preparation of Feedstocks

3.2.1 Preparation of RBD-PO and WPCO

RBD-PO as in Figure 3.1 was directly used for transesterification with methanol without any pre-treatment.

Figure 3.1 Refined, bleached and deodorized palm olein.

WPCO was allowed to settle for 3 - 4 days for impurities to sink at the bottom and proceed with filtered it using a laboratory scale vacuum to remove any visible proteins and other separate solids. The WPCO from UMP cafeteria before and after filtration is shown in Figure 3.2.



(a)

(b)

Figure 3.2 Waste palm cooking oil (a) before pre-treatment and (b) after pre-treatment

3.2.2 Preparation and Determination of Oil in Spent Bleaching Clay

The SBC was dried in an oven at 110 ℃ for 2 h. Next, the dried SBC was grind and sieved to obtain a smaller particle size (200 mesh).

(a) Extraction of oil absorbed in spent bleaching clay using soxhlet extraction

Residual oil from spent bleaching clay was extracted using Soxhlet with various solvents include *n*-hexane, petroleum ether and mix *n*-hexane:PE (50:50). The method was adapted with modification from Ahmad et al. (2001). Approximately 30 g SBC sample was weighed in Soxhlet thimble with about 6 g of fine sand or rock (to improve solvent drainage). A layer of cotton wool was used to cover the mixture for ease of solvent distribution. The thimble was then placed in the Soxhlet butt tube and extracted with 60 ml of co-solvent. In this study, the extraction solvent was collected for 3 h, there was no increment in weight of product after 3 h as depicted in Figure 3.3.

Figure 3.3 Oil extracted from spent bleaching clay

The yellow-brown supernatant layer was transferred into a pre-weighed flask, rotary evaporation was used to remove the co-solvent. The experiment was repeated three times for different type of solvents. The percentage of oil content was calculated using equation 3.1:

$$\text{Oil content (\%)} = \frac{M_1 \times 100}{M_0} \qquad 3.1$$

where M_1 is the mass of SBC oil extracted in gram.

M_0 is the mass of SBC sample used in gram.

(b) Extraction of oil absorbed in spent bleaching clay using ultrasound assisted

Oil content was determined by extracting 30 g dried SBC with 15 g each of petroleum ether and hexane (1:1, wt./wt.). The mixture immersed in an ultrasonic water bath (Bransonic at a working frequency of 42 kHz with 235 W power supply). The temperature was set at 60 ± 2 ℃ for 30 min. The sonicated mixture was then centrifuged for 5 min at 1000 rpm form a yellow-brown supernatant layer.

The yellow-brown supernatant layer was transferred into a pre-weighed flask, rotary evaporation was used to remove the co-solvent. The procedure was repeated three times and the accumulated supernatant solution was evaporated. The oil content was calculated using formula in Eq. 3.1.

3.3 Characterisation of Feedstocks

3.3.1 Determination of Water Content

Water content determination of SBC was carried out using Karl Fischer method of titrator (Methrom, Switzerland). 0.5 g of oil sample was injected into the titrator vessel. Dried methanol was used as a solvent while Hydranal Composite-2 was used as a titrant. SBC water content was determined by heating balance (MX-50). 5 g sample solid was dried in measuring balance and temperature was set at 200 ℃ until get the constant weight.

3.3.2 Determination of Acid Value (PORIM Test Methods (p1), 1995)

Titration method was used to determine acid value. Approximately 20 g of oil (RBD-PO) was weighed into 250 ml Erlenmeyer flask. Next, 50 ml neutralised of isopropanol was added. The solution was heated on the hot plate to about 40 ℃, gently shake and standard potassium hydroxide solution was used to titrate with until the first permanent pink solution for 30 s. The determination was done in triplicate. The acid value was calculated using the formula expressed in equation 3.2:

$$\text{Acid value (mg KOH/g sample)} = \frac{56.1 \times V \times M}{m} \qquad 3.2$$

where V is the volume of standard potasium hydroxide in ml

M is the molar concentration of standard potassium hydroxide used

m is the weight of sample in gram

Firstly, the potassium hydroxide was standardized with potassium hydrogen phthalate, the procedure as follows: The potassium hydrogen phthalate was dried in an oven at 120 ℃ until constant. About 0.4 of potassium hydrogen phthalate was weighed and directly pour into conical flask with 50 ml water and phenolphthalein indicator. The normality of the alkali was calculated with equation 3.3:

$$\text{Normality of the alkali} = \frac{W \times 10^3}{V \times 204.2} \qquad 3.3$$

where W is the weight of potassium hydrogen phthalate

V is the volume of potassium hydroxide in ml

For neutralisation of isopropanol, 50 ml of isopropanol is poured in the Erlenmeyer flask, heated on the hot plate, added 0.5 ml of phenolphthalein and neutralised by addition of 0.1 N potassium hydroxide drop wise until obtaining a faint, but permanent pink colour. The procedure was repeated for determination of acid value of WPCO and SBC oil.

3.3.3 Determination of Free Fatty Acid (PORIM Test Methods (p1), 1995)

The free fatty acid of feedstock was determined using the process described in section 3.3.12, the determination was done in triplicate. The free fatty acid of SBC oil was calculated using the following equation 3.4:

$$\text{Free fatty acid (\% as palmitic acid)}: \frac{25.6 \times N \times V}{W} \qquad 3.4$$

While, the free fatty acid content of RBD-PO and WPCO was expressed as percentages of oleic acid by the equation 3.5:

$$\text{Free fatty acid (\% as oleic acid)}: \frac{28.2 \times N \times V}{W} \qquad 3.5$$

where N is the normality of a standard potassium hydroxide solution
V is the volume of standard potassium hydroxide solution in ml.
W is the weight of sample in grams

3.3.4 Determination of Density

The density meter Kyoto-kem DA-640 was used to determine the density measurement at temperature of 311.5 + 0.05 K.

3.3.5 Determination of Viscosity

The viscometer Brookfield DV-II+Pro was used to determine viscosity of oil and methyl ester.

3.3.6 Determination of Iodine Value

About 0.4 g sample was weighed in 500 ml flask. 20 ml of cyclohexane was slowly added into the sample function as to dissolve the oil. Stopper was inserted immediately after 25 ml of Wijs solution was added. The flask was shaken gently and placed for 1 h in dark.

Next, 100 ml of water and 20 ml of potassium iodide solution (15 %) were added. The solution was titrated until the yellow colour had almost disappeared by using sodium thiosulphate solution. Starch solution was added about 1 - 2 ml and the titration is continued until blue colour disappeared after very vigorous shaking. A blank test (without sample) was carried out simultaneously (PORIM test method, 1995). The determination was carried out in duplicate. Iodine value then calculated by using the following formula in equation 3.6.

$$\text{Iodine Value: } \frac{12.9 \times \text{N} \times (\text{V2} - \text{V1})}{\text{W}} \qquad 3.6$$

where N is the normality of the sodium thiosulphate solution

V2 is the volume of sodium thiosulphate solution in ml used for the blank test

V1 is the volume of sodium thiosulphate solution in ml used for the sample determination

W is the weight of sample on gram.

3.3.7 Deterioration of Bleachability Index Analysis

Deterioration of Bleachability Index (DOBI) is an indication of the bleachability of the crude palm oil based on the amount of carotenes still present in the crude oil and the amount of secondary oxidation products (Siew, 1994). A good easily bleached crude palm oil will have a DOBI of 4, while average quality crude will exhibit a DOBI of 2.5 to 3. Table 3.1 below, shows the refinability of CPO according to DOBI values. Discriminant function (DF) is expressed by Y to describe the quality and categories of palm oil.

Table 3.1

Refinability of CPO according DOBI values

Y	**DOBI**	**Grade**
<0	<1.7	Poor
1-10	1.8-2.3	Fair
11-20	2.4-2.9	Good
21-25	3.0-3.2	Very good
>25	>3.3	Excellent

Source: Siew (1994)

UV-visible spectrophotometer can be used to measure DOBI and it is a numerical ratio of spectrophotometric absorbance at the wavelength at 446 nm to absorbance at 269 nm. The measurement was carried out on 1% concentration solution of crude palm oil in isooctane. The experimental procedures for the determination for DOBI value are as follows (Boey et al., 2011a).

About 0.1 g of completely melted and homogenised crude palm oil sample was weighed into 25 ml volumetric flask. Dissolve in *n*-hexane (0.5 – 1.0 % concentration) and make-up to the desired volume. Fill up 10 mm cuvettes with oil solution and measure its absorbance by using spectrophotometer at 269 nm and 446 nm against pure solvent. The DOBI value was calculated using the equation 3.7 :

$$\text{DOBI} = \frac{Abs\ 446}{Abs\ 269}\ (in\ a\ 10\ mm\ quartz\ cell) \qquad 3.7$$

3.3.8 ICP-MS Analysis

This analysis was done to study the leachability of catalysts by measuring the element composition in the leachate sample. About 0.5 mL sample was pipette and diluted in 30% of nitric acid. After setting the required method, the sample was proceeded to run on ICP-MS (Agilent 7500 CX) instrument. For operations with three or less vessels, power used is simultaneously up to 500 Watt. The maximum power for the microwave program is 1500 W for Ethos and 1200 W for start units.

3.4 Catalysts Preparation for Transesterification

3.4.1 Deoiled SBC as a Catalyst Support in Transesterification

Spent bleaching clay (SBC) was obtained and dried in an oven at 105 °C until constant weight in order to remove water. Subsequently, the dried SBC was ground and sieved to get a smaller particle size. After oil extraction, the deoiled SBC was then calcined (500 °C) with furnace to remove the remains of carbon and other impurities. For this study, an electrical furnace (Nabertherm) was used, and the obtained catalyst support was labelled as deoiled-SBC (DSBC) as in Figure 3.4 below.

Figure 3.4 Deoiled spent bleaching clay.

3.4.2 Potassium Doped onto DSBC as a Catalyst in Transesterification

The typical procedure for the impregnation of the sample was involving the placement of 3 g of DSBC into a 250 ml flask held in an ultrasonic water bath. The K-functionalized D-SBC samples were prepared at 40 wt.% of KOH. DSBC particles with KOH were dried in a vacuum oven at 120 °C for 16 h. Upon drying, the DSBC particles with KOH were calcined at 500 °C for 4 h and being depicted in Figure 3.5. The catalyst was calcined to remove the remaining carbon and other impurities.

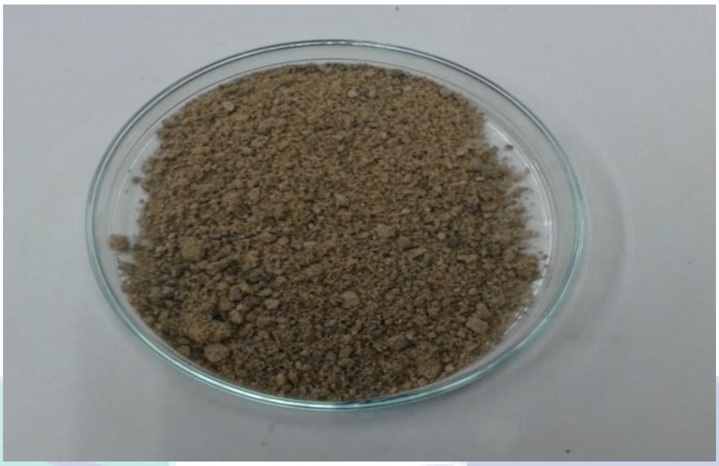


Figure 3.5 Potassium doped onto DSBC.

3.4.3 Calcium Doped onto DSBC as a Catalyst in Transesterification

The typical procedure for the impregnation of the sample was involving the placement of 3 g of DSBC into a 250 ml flask held in an ultrasonic water bath. The Ca-functionalized DSBC samples were prepared at 40 wt.% using commercial CaO. DSBC particles with CaO were dried in a vacuum oven at 120 ℃ for 16 h. Upon drying, the DSBC particles with CaO were calcined at 500 ℃ for 4 h and the catalyst is shown in following Figure 3.6. The catalyst was calcined to remove the remains of carbon and other impurities.

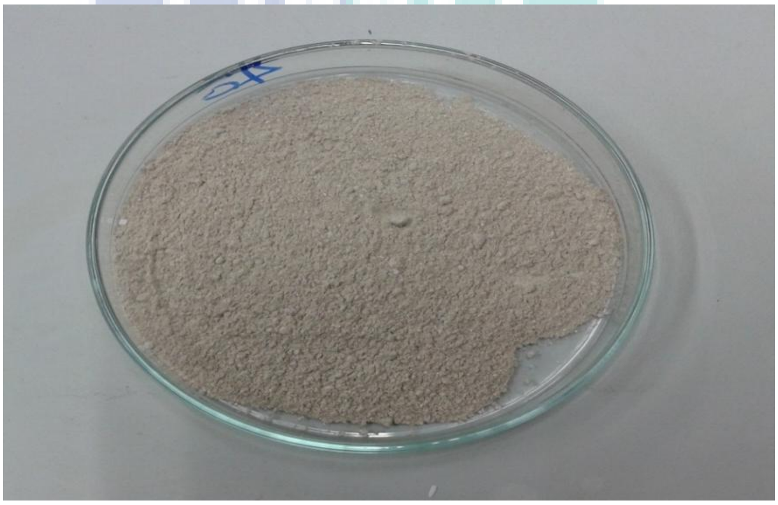


Figure 3.6 Calcium doped onto DSBC.

3.4.4 Lanthanum Doped onto DSBC as a Catalyst in Transesterification

The typical procedure for the wet impregnation of the sample was involving the placement of 3 g of DSBC into a 250 ml flask held in an ultrasonic water bath. The La-functionalized DSBC samples were prepared at 40 wt.% of $LaCl_3$. La-functionalized DSBC particles were dried in a vacuum oven at 120 ℃ for 16 h. Upon drying, the DSBC particles doped La were calcined at 500 ℃ for 4 h. The catalyst was calcined to remove the remains of carbon and other impurities. La-functionalized DSBC catalyst is shown in Figure 3.7.

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Figure 3.7 Lanthanum doped onto DSBC.

3.5 Catalysts Characterization

3.5.1 TGA Analysis of the Catalysts

About 7 mg of catalyst instrument from 25 to 900 ℃ with 10 ℃/min heating rate, under N_2 environment. was examined by thermogravimetric analysis (TGA) using the Mettler Toledo TGA/DTA 851e.

3.5.2 BET Analysis of the Catalysts

The surface analysis of the catalysts was carried by Micromeritics ASAP 2000. The sample was degassed at 105 ℃ prior to analysis and the adsorption of N_2 was measured at -196 ℃. The surface area was calculated using Brunauer-Emmett-Teller (BET) equation over the pressure rangeof $P/P_o = 0.01 - 0.30$, where a liner relationship was obtained.

3.5.3 XRD Analysis of the Catalysts

This by X-Ray Diffraction techniques was based on the fact that every crystalline material has its own characteristic diffractogram. XRD patterns were identified by X-ray diffraction (Rigaku) with CuKα radiation in the range of 2θ from 2 ° to 60 ° at a scanning speed of 3 ° per minute. All the samples were fully dried before XRD diffactograms were measured.

3.5.4 FTIR Analysis of the Catalysts

The Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer Spectrum 100) was used to investigate the functional groups of catalysts. Each waste catalysts sample was mixed with standard KBr technique. The samples were then scanned transmittance mode from 400 to 4000 cm^{-1}. All spectra were referenced against the background spectrum.

3.5.5 FE-SEM and EDX Analysis of the Catalysts

The catalyst morphology was observed by FE-SEM ZEISS (EVO50) together with Energy Dispersive X-ray (EDX).

3.5.6 XRF Analysis of the Catalysts

X-ray fluorescence (XRF) analysis was performed on Bruker, S8 Tiger using pressed-pellet (pressure at 8.0 Pa) method. The purpose of this analysis is to study the composition of the catalyst.

3.5.7 Basicity Analysis of the Waste Catalysts using Hammett Indicators

Base strengths of the catalyst were determined by using Hammett indicators. The following Hammett indicators were used: phenolphthalein (H_= 8.2), 2,4-dinitroaniline (H_= 15.0) and 4-nitroaniline (H_= 18.4). About 25 mg of catalyst was shaken with 1 mL of a solution of Hammett indicator diluted with methanol, and left to equilibrate for 2 h. After the equilibration, the colour change of the solution was noted.

3.6 Transesterification Reaction

The transesterification of feedstock (i.e.: RBD-PO, WPCO and SBC oil) into biodiesel using waste catalyst was carried out in a 50 ml one-neck round bottom flask equipped with reflux condenser, thermometer, and magnetic heating mantle, as shown in Figure 3.8. In a typical reaction, 5 g of oil was added in round bottom flask onto mixture of calcined catalyst and methanol. The transesterification experiments were carried out at temperature 65 ℃ and stirred vigorously for 3 h. Reaction parameter (catalyst amount (1-7 wt.%), methanol to oil molar ratio (3:1-15:1) and reaction time (1-7h)) were varied to identify the best conditions.

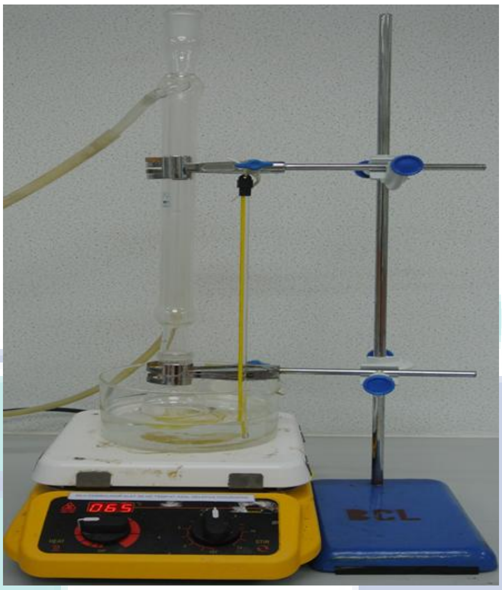


Figure 3.8 Transesterification reaction set-up.

The resultant mixture was then cooled to room temperature. Successful transesterification reaction produced two liquid phases: methyl ester and crude glycerine, the heavier crude glycerine was settled at the bottom. Another way is addition of *n*-hexane to ease the separation process, the glycerine, unreacted methanol and residue of catalyst was settled in the bottom and methyl ester, *n*-hexane and oil unreacted is settled up. The methyl ester content was quantified using GC-MS and GC-FID.

3.7 Analysis of Methyl Ester

3.7.1 Qualitative Analysis of Methyl Ester

In order to ensure the completeness of transesterification process, the qualitative analysis was utilized using Thin Layer Chromatography (TLC). TLC was performed on an aluminium sheet coated with silica gel 60 (DC- Fertigplatten Kieselgel 60 F254). A solvent mixture from chloroform and petroleum ether (with ratio 3:2) was used as evolving solvent and for visualization of the spots, iodine vapour was used. The achievement of reaction was judged by the disappearance of triglyceride spots and the formation of methyl esters. The spot of mixture internal standard methyl heptadecanoate

(C_{17}) and oil was used as a comparison for the methyl ester formation, as shown in Figure 3.9.

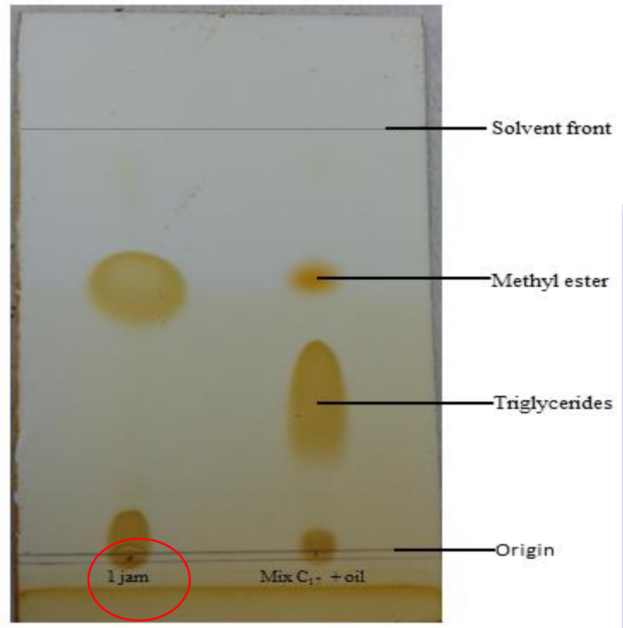


Figure 3.9 TLC plate showing of methyl ester and mixture standard C_{17} and oil in 1 h, using potassium doped on d-SBC as a catalyst and RBD-PO as a feedstock.

3.7.2 Quantitative Analysis of Methyl Ester

The methyl ester content in biodiesel was determined using gas chromatography-flame ionization detector (GC-FID) method. In this study, GC-FID (Agilent 7890A) with capillary column DB-wax (length 60 m × diameter 0.25 mm × film thickness 0.25 µm) and a flame ionization detector operated at 300 ℃ was used. Helium was used with a linear velocity of 40 cm/s as the carrier gas. The injector temperature was 250 ℃ and at split ratio of 60:1. The initial oven temperature was 190 ℃ with an equilibration time of 2 min. After isothermal period, the oven temperature was increased to 230 ℃ at a heating rate of 10 ℃/min and held for 8 min. About 20 mg of methyl ester sample was weighed in a vial and added of 400 µL of internal standard dilute in heptane 10 mg/ml concentration. The vial was then shaken well to homogenous mixture. Sample volume of 1 µL was injected into GC. The methyl ester content of biodiesel was calculated by following the European regulation procedure EN

14103 and using methyl heptadecanoate as an internal standard. The methyl esters content was calculated using the following formula:

$$\text{Methyl ester content (\%)} = \frac{A_{total} - A_{ISTD}}{A_{ISTD}} \times \frac{C_{ISTD} \text{ x } V_{ISTD}}{W_{sample}} \times 100\% \qquad 3.8$$

where A_{total} is the total peak area of methyl esters

A_{ISTD} is the area of methyl heptadecanoate

V_{ISTD} is the volume of methyl heptadecanoate

C_{ISTD} is the concentration of methyl heptadecanoate

W_{sample} is the weight of sample

3.8 Reusability, Regeneration and Leaching Study of Waste Catalysts

In order to examine the potential reusability of the catalyst, used catalyst was tested for its catalytic activity. For reuse experiments, the used solid catalyst that recovered by centrifugation was regenerated by washing with methanol followed by hexane. The dried used catalyst at 105 ℃ for overnight, then directly used as a catalyst for the repeated reactions. For the regeneration catalysts, after washing, the catalysts were calcined at 400 ℃ of 5 h.

The leaching study was carried out in this study. The calcined catalyst was placed in contact with methanol and kept under stirring conditions at 65 ℃ for 1 h. Then, the stirring was stopped, the catalyst was decanted, and the treated methanol was placed in contact with feedstocks. In other words, the transesterification reaction was carried out without catalyst.

3.9 Transesterification Using Ultrasound Irradiation and Mechanical Stirring Methods

Transesterification reaction was carried out in a 250 ml three-neck round bottom flask equipped with reflux condenser, thermometer, and magnetic heating mantle, with the constituent of 10 g SBC (1.35 g oil, at oil content 13.5 wt.%), 40 wt.% catalyst (0.27

g, based on oil weight), 5.85 g of methanol to give the molar ratio of methanol to oil of 15:1. The transesterification experiments were carried out at temperature 65 ℃ and stirred vigorously for 1 h.

The resultant mixture was then placed in a test tube and centrifuged at 6000 rpm for 5 min. Three layers were formed; the top was glycerol, followed by methyl esters and the bottom part is the used catalyst. Pure ME was obtained upon solvent evaporation with aid of hexane in fume hood). The resultant ME was subjected to chromatographic analysis for quantification using GC-FID (Agilent 7890A) following the European procedure EN 14103.

3.10 Fuel Properties Determination of The Methyl Ester Products

The fuel properties of methyl ester such as density, viscosity, flash point, heating value, cloud point and sulphur content is determined. The density and viscosity procedure is presented in section 3.3.5 and 3.3.45.

3.10.1 Determination of Flash Point

Flash point is the measure of flammability of a fuel. Higher flash point ensures safer storage and transportation of the fuel. The flash point is defined as the minimum temperature at which a fuel produces sufficient vapor to ignite momentarily and give the first flash. Petrotest PM4: Close cup Pensky-Martens apparatus was used to determine flash point using ASTM method D 93.

3.10.2 Determination of Higher Heating Value

Higher heating value (HHV) of biodiesel was measured using IKA C-200 oxygen bomb calorimeter using ASTM D240. Approximately 0.2 g of biodiesel was placed into a quartz crucible inside the combustion chamber. Pure oxygen gas was introduced into the chamber until 30 bar pressure was achieved. Two litres of tap water at temperature range of 20 – 23 ℃ was added inside the calorimeter surrounding the chamber. After five minutes of stirring, the water temperature became stable and the samples were ignited. The changes in water temperature were monitored until it remained constant. Differences of initial and final temperature were used to calculate the heating value of the samples. The calorimeter heat capacity was calibrated using benzoic acid as reference.

3.10.3 Determination of Cloud Point

Biodiesel cloud point measure is based on ASTM D2500. The biodiesel inside to cool batch until a temperature is reached where the sample shows no movement after 5 s.

3.10.4 Determination of Sulphur Content

The sulphur content of biodiesel was determined using C, N, O, S analysis. The composition of C, H, S and N elements in biodiesel were determined by Elementar CHONS Analyzer. The oxygen content of biodiesel was not included in this analysis.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Characterization of Feedstocks

4.1.1 Characteristics of RBD-PO, WPCO and SBC Oil

The characterization results of feedstock RBD-PO, WPCO and SBC oil in term of acid value, free fatty acid (FFA), water content, density, viscosity are presented in Table 4.1. As stated, SBC oil has the highest acid value, FFA and water content compared to WPCO and RBD-PO. Higher acidity in SBC oil (8.55 mg/KOHg) is justified since it consists of crude palm oil which contains comparatively higher FFA, the reported range of free fatty acid content of crude palm oil was 2.3–6.7% (Saad et al., 2007, and Tan et al., 2009). However, the relatively high moisture content in CPO may be related with heating duration of palm fruit and the quantity of water added during boiling process. In contrast, the RBD-PO used in this study has very low acid value (0.16 mg/KOHg) and FFA (0.08 %); obviously RBD-PO is refined through a number of processes until it reached FFA of 0.08 % (Refaat, 2011), in agreement with PORIM standard specifications for processed palm oil, the FFA content of RBD-PO should be lower than 0.1% (Tan et al., 2009). Meanwhile, WPCO and SBC oil FFA contents are 1.56 % and 1.92 % respectively. The WPCO from RBD-PO has higher FFA at 2.95 mg/KOHg. This could be the result of the heat and water which accelerate the hydrolysis of triglycerides during the frying process, eventually increases the FFA content and water content in the oil (Marmesat et al., 2007). For the moisture content, RBD-PO gives 0.09 wt.%, WPCO gives 0.14 wt.% and O-SBC gives 0.11 wt.% respectively. The density of feedstock is almost the same which is around 0.90-0.91

g/cm^3 which is in an acceptable range. Next, SBC oil gives the lowest viscosity which is 25.10 cP, followed by RBD-PO (56.60 cP) and WPCO (60.20 cP).

Table 4.1

Properties of the oils

		Composition (%)		
Test	**Unit**	**RBD-PO**	**WPCO**	**SBC Oil**
Acid value	(mg/KOHg)	0.16	2.95	8.55
FFA	(%)	0.08	1.56	1.92
Water content	(wt.%)	0.09	0.14	0.11
Density	(g/cm^3)	0.91	0.91	0.90
Viscosity	(cP)	56.60	60.20	25.10

Table 4.2 presents the characterization of WPCO from different sources where WPCO$_1$ is from Sinar Mesra Seafood Gambang, WPCO$_2$ is from Suraya Tomyam Gambang and WPCO$_3$ is from Andaman Tomyam Gambang. Although the WPCOs were from different origins, they were quite similar to each other, with the exception of the acid value, FFA and viscosity which were different. Many other researchers have linked for this case with the process itself, such as temperature, duration heating, heating pattern (continuous or intermittent), turnover rate and also for the food subjected at frying, i.e. lipid composition, will change some physical and chemical properties (acid value and FFA content) in oil after frying (Machado et al., 2007, and Refaat, 2011). However, continuously using the same oil or fat for frying will change physical properties in the oil, such as (i) an increase in viscosity, (ii) an increase in specific heat, (iii) a decrease in surface tension, and (iv) the colour tends to be darker (Cvengroš and Cvengrošova, 2004).

Table 4.2

Properties of WPCO from various sources

Test	**Unit**	**WPCO$_1$**	**WPCO$_2$**	**WPCO$_3$**	**Present work**
Acid value	(mg/KOHg)	4.77	6.69	2.51	2.95
FFA	(%)	2.39	3.36	1.23	1.56
Water content	(wt.%)	0.12	0.12	0.12	0.14
Density	(g/cm^3)	0.91	0.91	0.91	0.91
Viscosity	(cP)	68.20	69.20	67.6	60.20

The compositions of fatty acid of RBD-PO are reported in Table 4.3. The most abundant fatty acid is the oleic acid, the similar observation was reported by (Rustan and Drevon, 2005) and (Lam et al., 2010). RBD-PO has long been investigated as a feedstock in the production of biodiesel (Kansedo et al., 2009, and Noiroj et al., 2009), especially in Indonesia and Malaysia which are the major palm oil producing countries in the world. RBD-PO used in this study contains 42.5 % saturated and 57.5 % unsaturated fatty acids.

Similar to RBD-PO, the palm olein is the major composition of WPCO used in this study, as WPCO is probably derived from the virgin RBD-PO. The properties of WPCO are presented in Table 4.3, in which higher content of unsaturated fatty acid is (66.3 %) and contain 33.7 % of saturated fatty acid. The composition of fatty acid in WPCO resembles the composition of chicken fat. The WPCO might be used to fry chicken which justify the presence of palmitoleic acid ($C_{16:1}$). Originally in RBD-PO the palmitoleic acid is not usually present.

Table 4.3

Fatty acid composition of RBD-PO and WPCO

Fatty acid	**Composition (%)**	
	RBD-PO	**WPCO**
	Present work	**Present work**
Saturated		
Lauric ($C_{12:0}$)	0.1	0.9
Myristic ($C_{14:0}$)	1.0	1.0
Palmitic ($C_{16:0}$)	37.1	28.2
Stearic ($C_{18:0}$)	4.3	3.6
Sub total	42.5	33.7
Unsaturated		
Myristoleic ($C_{14:1}$)	-	-
Palmitoleic ($C_{16:1}$)	-	4.6
Oleic ($C_{18:1}$)	45.4	42.4
Linoleic ($C_{18:2}$)	11.9	18.3
Linolenic ($C_{18:3}$)	Traces	1.0
Arachidic ($C_{20:0}$)	0.2	Traces
Gardoleic ($C_{20:1}$)	-	-
Sub total	57.5	66.3
Total	100.0	100.0

Table 4.4

Fatty acid composition of SBC oil

	Composition (%)	
Fatty acid	**Present work**	**Previous work** (Lim et al., 2009)
Saturated		
Lauric ($C_{12:0}$)	4.0	4.5
Myristic ($C_{14:0}$)	2.8	2.6
Palmitic ($C_{16:0}$)	43.9	41.1
Stearic ($C_{18:0}$)	4.4	4.6
Sub total	55.1	52.8
Unsaturated		
Oleic ($C_{18:1}$)	34.6	37.5
Linoleic ($C_{18:2}$)	10.3	9.7
Arachidic ($C_{20:0}$)	traces	traces
Sub total	44.9	47.2
Total	100.0	100.0

The feedstock compositions were determined by using gas chromatography - mass spectrometry (GC-MS). From the composition in following Table 4.4, noted that the major fatty acid in the SBC oil is palmitic acid (43.9%), the acidity is reported with respect to palmitic acid. The result shown is comparative to Lim et al. (2009). The composition of fatty acids in SBC oil is presented in Table 4.4. The fatty acid distribution of SBC oil has higher saturated components than unsaturated fatty acids. From the data, SBC oil used in this experiment has higher palmitic acid content (43.9 %, Table 4.4). In contrast, CPO generally contains less than 1% of lauric acid. This inconsistency may arise due to the adulteration of the SBC in the refinery with palm kernel oil. Commonly, palm kernel oil content is of 4.0-8.0% of lauric composition. With about 55.1% of the fatty acid being of the saturated type, the remaining 44.9% of the content is accounted for unsaturated fatty acids.

4.1.2 Characteristics of SBC and Extraction of SBC Oil

Among the waste vegetable oils, animal fats and biomass sources, waste cooking oil have attracted much attention as a potential resource for production of an alternative for petroleum-based diesel fuel. A large range of industrial wastes, both natural and synthetic, are disposed without extracting the useful components from them. Biomass is a promising source of renewable energy that contributes to energy needs and is the best alternative for guaranteeing energy for the future. The previous investigated of spent bleaching clay (SBC) as a waste biomass from palm oil refinery was promising and successful as a feedstock in transesterification (Lim et al., 2009; Huang and Chang, 2010, and Mat et al., 2011).

In order to utilize the residual oil from SBC, the adsorbed oil has to be extracted first. For that purpose, the Soxhlet extraction method was conducted by using non-polar solvent which is *n*-hexane. The best amount of the residual oil extracted from SBC by *n*-hexane is only 25.53 ± 0.23%, which was comparable with those reported in literature (Loh et al., 2013 and Khang et al., 2014). The residual oil recovered from SBC via n-hexane extraction is dark brown in colour. It is transparent and has no deferred solids. Soxhlet extraction gave the highest oil recovery with *n*-hexane as best solvent. Meanwhile, the mechanical stirring extraction method gave lowest oil content (18.73 ± 1.81 wt.%) compared to other methods. A mechanical stirrer (Wisestirr, 83 W, 230V, 50/60 Hz) is used for extraction. This is because the mechanical stirrer technique requires more speed which calculated as one of the important parameters for this extraction method.

The other characteristic that is deterioration of bleachability index (DOBI) analysis indicates the deterioration of the oil quality. Table 4.5 shows that the DOBI value of residual oil extracted using non-polar solvents are higher than polar solvents. According to the DOBI values and respective oil quality set by then Palm Oil Research Institute of Malaysia (Siew, 1994; tabulated in section 3.3.7), methanol recorded the lowest DOBI index of 1.5 (poor), followed by ethanol (2.1; fair), then petroleum ether (2.8; good) and same index for both *n*-hexane and mixed *n*-hexane:PE (3.3; excellent). The dominant solvent in extracting oil from SBC is *n*-hexane. Basically, oil is attracted to non-polar solvent because the electronegativity and the bonds between carbon and hydrogen in *n*-hexane are uniform. Due to the hydrophobic character of oil itself, it is not attracted to polar solvents such as methanol. Therefore, the use of n-hexane shows the higher oil extraction because of it provides ideal functionality as an extraction solvent for oils in terms of oil solubility and ease of recovery.

Table 4.5

DOBI analysis of SBC oil with different solvents extracted by Soxhlet

Solvent for extract SBC Oil	**DOBI Index**	**Oil Grade (Siew, 1994)**
Methanol	1.5	Poor
Ethanol	2.1	Fair
Petroleum Ether	2.8	Good
n-hexane	3.3	Excellent
Mix *n*-hexane:PE	3.3	Excellent

The ultrasound irradiation (CPX3800H, Branson 3800) with constant frequency of 40 kHz as a different method of oil extraction from spent bleaching clay was also investigated at temperature of 68.5 °C. The amount of oil extracted from spent bleaching clay with *n*-hexane as a solvent for 1 h was at 20.17 ± 0.11 wt.%. It is concluded that, ultrasound promises simpler process with higher product and the process can be completed in shorter reaction time compared to Soxhlet extraction methods. The higher efficiency of the extraction process using ultrasound has previously been reported by Li et al. (2004) in extraction soybean oil using mix *n*-hexane:isopropanol. The oil extraction capabilities of *n*-hexane:isopropanol mixture was 5.2 % higher than *n*-hexane alone.

4.2 Catalyst Characterisation

4.2.1 TGA Analysis of the Catalysts

TGA was conducted in order to assess the thermal stability and the decomposition profile of the catalysts. The thermal analysis of K-DSBC, Ca-DSBC and La-DSBC is depicted in Figure 4.1 A, B and C which shows three decomposition steps.

The first stage of degradation occurred from 50 ℃ to 180 ℃. The weight loss of the K-DSBC is 1.1 % which is from 99.9 % to 98.8 %. The first stage for Ca-DSBC was observed at the temperature range of 40 ℃ to 150 ℃. The weight loss of 4.3 % taken placed at this stage which is 99.8 % - 95.5 %. Meanwhile for La-DSBC, the first decomposition happened at 20 – 100 ℃ and loss of 3.9 % (99.9 % to 96.0 %) is observed. This degradation stage is due to the remove of the water molecules and other small volatile molecules absorbed on the catalyst surface and inside the pores. The water molecules present may due to water added during the wet impregnation process and absorption of the water molecules in the air.

The second stage of degradation occurred from 180 ℃ to 650 ℃. The weight loss of the catalyst for this stage is 98.8 % to 97.5% which is 1.3 %. This may due to the combustion of organic matter and silicate layer dehydroxilation. KOH reacted with carbon dioxide in this stage to form potassium carbonate and water. The second stage of Ca-DSBC shows about 5% (95.5 % -90.5 %) of weight loss which occurred in the temperature range of 150 ℃ to 630 ℃. The loss for La-DSBC is 3 % for this stage (96.0 to 93.0 %) which is in 100 ℃ to 600 ℃. It could be due to the loss of organic compounds known as decomposition of organic components or due to possible rearrangement in the structural arrangement within the compound itself. A study by Meng et al. (2006) explained that a series of chemical and physical reactions took place that resulted the removal of functional groups (e.g., C=O and CH_3) and the release of gaseous substances (e.g., CO_2, CO, CH_4 and H_2).

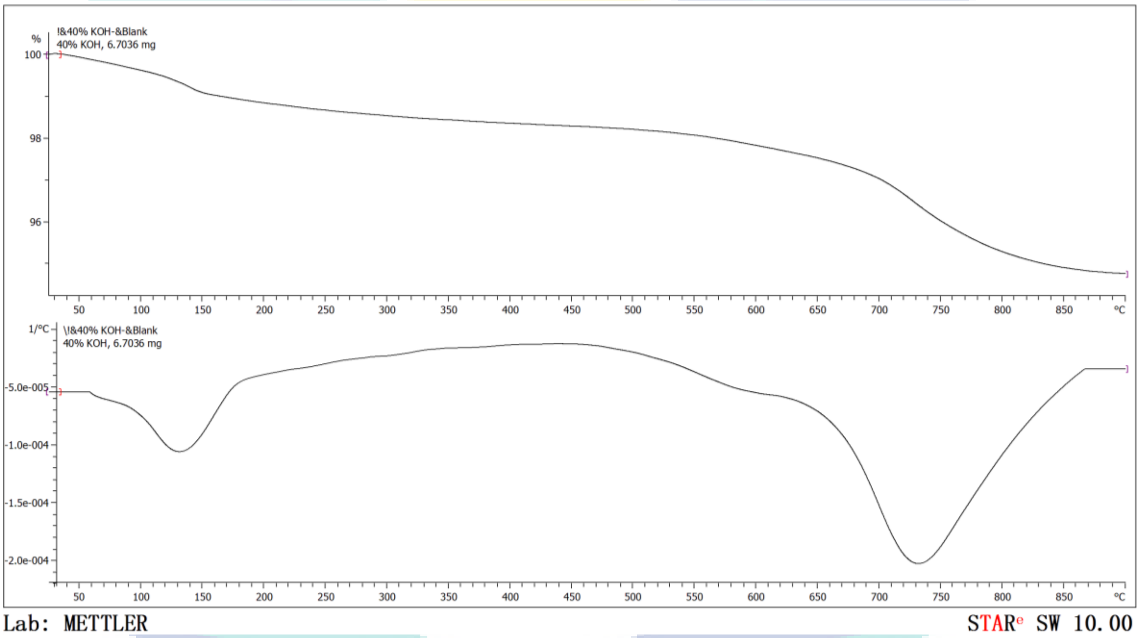
$$2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Third stage of degradation occurred at 650 ℃ to 900 ℃. The weight loss in this stage is from 97.5 % to 95.0 % which is 2.5 %. This is due to loss of hard bound water from silanol group in order to form silicate and siloxane bond with K^+. During this stage, the equation below happened.

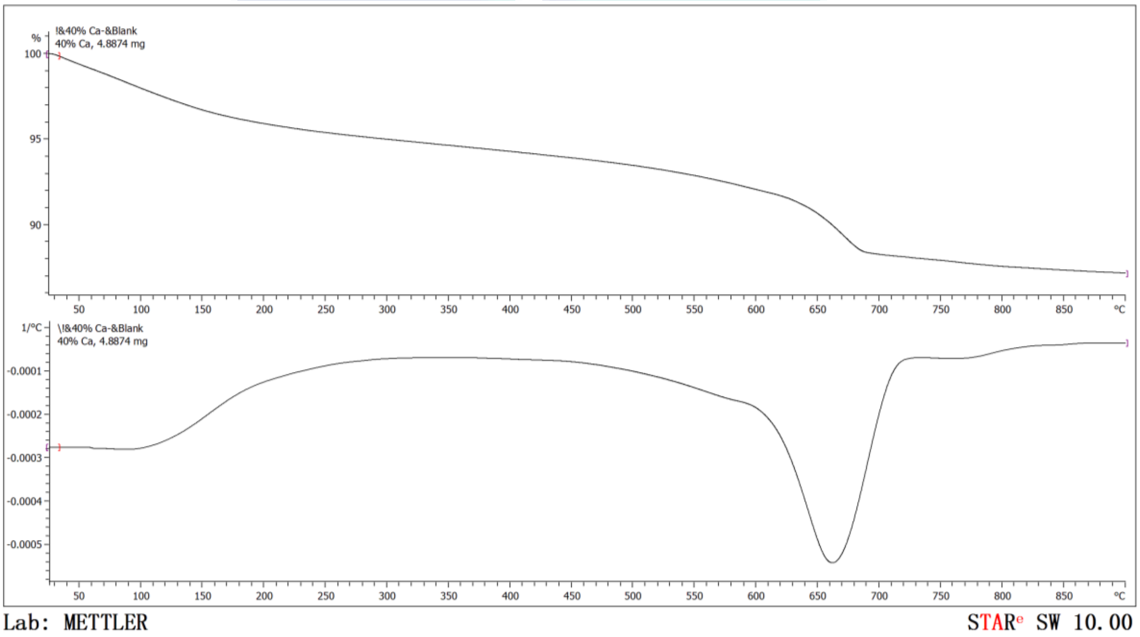
$$K_2CO_3 \longrightarrow K_2O + CO_2$$

While for Ca-DSBC produced by further carbonization and structural rearrangement and was observed in the temperature range of 630 ℃ to 730 ℃. The weight loss of 2.0 % (90.5 % - 88.5 %) occurs at this stage due to the CO_2 release. After the temperature at 730 ℃, there was no loss of weight observed. The final stage for La-DSBC is in 600 ℃ – 740 ℃ and have weight loss about 9.0 % that is 93 to 84.0 %.

(A)



(B)



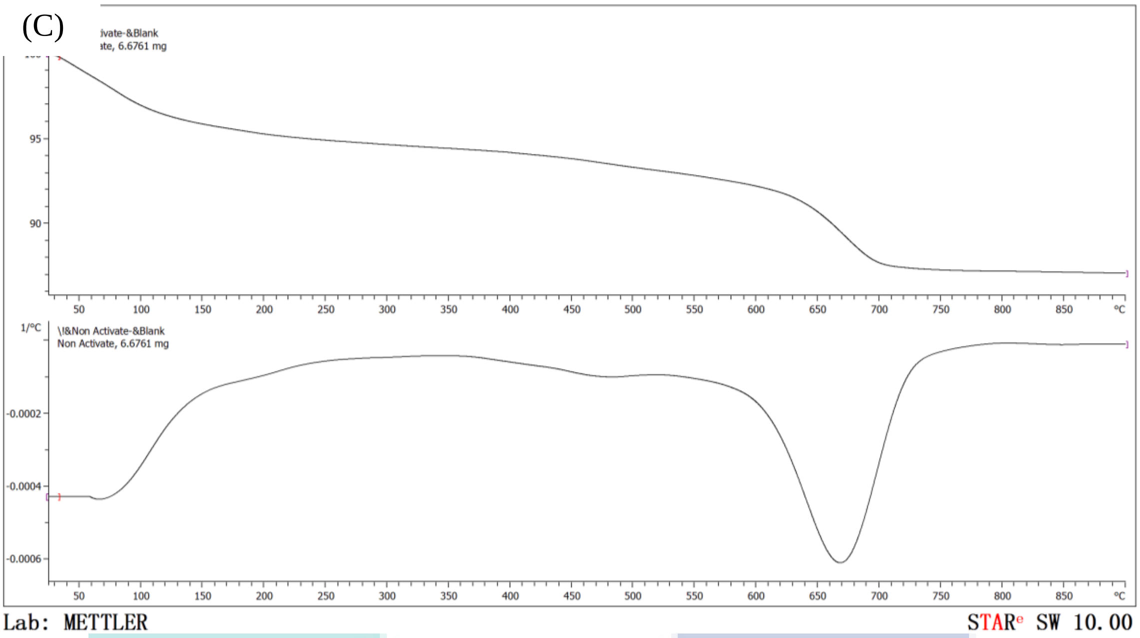


Figure 4.1 Thermogram of the catalysts (A) K-DSBC; (B) Ca-DSBC and (C) La-DSBC.

4.2.2 XRD Analysis of the Catalysts

The XRD analysis was employed to observe the crystal structure of the catalyst. The diffractograms of DSBC showed a minor amorphous structure as in Figure 4.2; with silicon dioxide as a dominant structure and other silicates (Yang et al., 2008). XRD analysis is carried out for D-SBC and the metal impregnated catalyst (K, Ca, La) in order to demonstrate that D-SBC is a good support material for metals to produce catalyst for transesterification.

In the XRD pattern of D-SBC shows that it contains high amount of SiO_2 proved that it is suitable to become the support for catalyst. After impregnation of the K^+, Ca^{2+} and La^{3+} species, the crystallinity of the catalyst increased. For D-SBC, the intense peak found at 21.014 ° and 26.838 °. SiO_2 appears at miller indices of (100) and (011) which are at 21.014 ° and 26.838 °.

For K-DSBC, the intense peak found at 20.04 °, 26.73 °, 29.04 ° and 40.368 °. SiO_2 appear at miller indices of (20-2) which are at 21.01 °. As depicted in Figure 4.2,

K_2MgSiO_4 can be seen as it shows at 20.04 °. On the other hand, $K_4CaSi_3O_9$ appears at miller indices (20-2) at 29.04 ° and $K_{9.6}Ca_{1.2}Si_{12}O_{30}$ is (-312) at 40.37 °. The calcined K-DSBC contains K_2O (potassium oxide) because of the KOH molecules were transformed into K_2O. K_2O believed as the significant molecule which play an important role during transesterification (Kusuma et al., 2013).

Next, Ca-DSBC and La-DSBC illustrate CaO and La_2O_3 peaks which give evidence to the metal impregnated onto DSBC. It is very likely that fine CaO and La_2O_3 particles are embedded in DSBC matrix, proposing that DSBC denotes the support for CaO and La_2O_3 as well as K_2O.

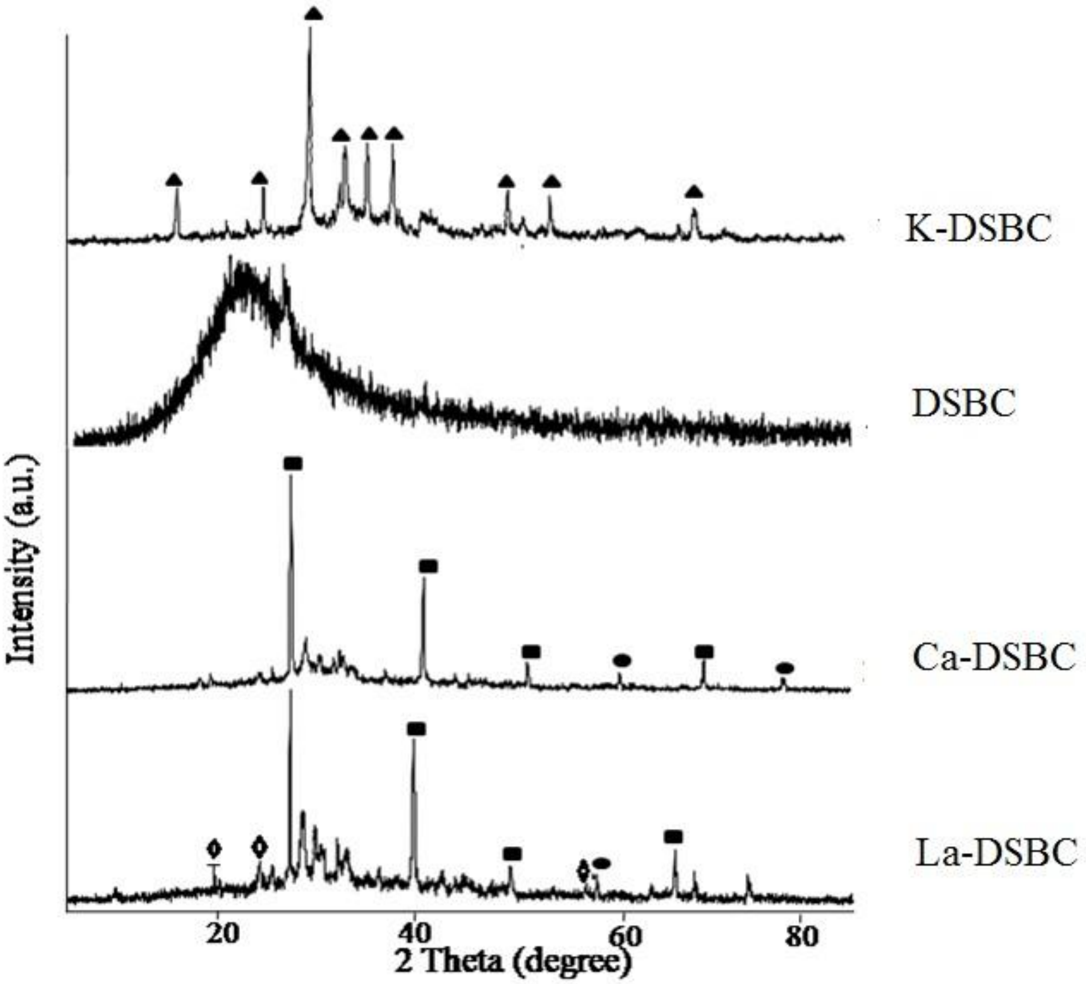


Figure 4.2 Powder XRD patterns of K-DSBC, Ca-DSBC, La-DSBC and SiO_2; ▲, K_2MgSiO_4 ♦, $K_{9.6}Ca_{1.2}Si_{12}O_{30}$ ◊, $K_4CaSi_3O_9$ ■, CaO □, La_2O_3.

4.2.3 Surface Analysis (BET Method) of the Catalysts

Brauner, Emmett and Teller (BET) method determines the pore structure and surface area of the catalysts.

The BET results showed great decrease in surface area, pore volume and pore size of K-DSBC which summarized in Table 4.6. The BET surface area for D-SBC is 24.3200 m^2/g, whereas the BET surface area of K-DSBC is only 8.0127 m^2/g. meanwhile for Ca-DSBC and La-DSBC is 10.3493 m^2/g and 8.1328 m^2/g. The higher surface area of deoiled SBC suggests a higher concentration of –O- and –OH- groups. The pore volume of D-SBC is 0.132820 cm^3/g, the pore volume decreased to 0.004616 cm^3/g after being impregnated with K. The same trend also goes to Ca-DSBC (0.002869 cm^3/g) and La-DSBC (0.003739 cm^3/g). The pore size also decreased from 218.4544 Å to 23.0439 Å for K-DSBC**.** While for Ca-DSBC also decreased to 32.2553 Å and La-DSBC is 25.0667 Å.

These characteristics obviously occur after impregnation of K, Ca and La into D-SBC. During the impregnation process, the K filled the available pore of the D-SBC molecules (Fadhil et al., 2016). As the pores of the D-SBC are being occupied, the total surface area of D-SBC decreases. The pore size also decreased due to impregnation of KOH, CaO and $LaCl_3$ into D-SBC. Some KOH probably transformed into K_2O after calcined and filled up the pore of the D-SBC hence lead to smaller pore size and volume, where the same phenomenon also occur towards Ca-impregnated and La-impregnated DSBC. The thermal activation resulted in much smaller particles as well as open up the pores on the surface catalyst. The relation is that when surface area increases, the pore size and pore volume will also increase. It is in line was documented with previous study by (Kouzu et al., 2009).

According to the 1985 IUPAC physisorption isotherms, the N_2 adsorption-desorption isotherm of the samples can be classified into type III isotherm (Sing et al., 1985). The slope of type III isotherm does not show the region for monolayer formation. The absorbate-absorbate interaction play significant role in this type of isotherm. The absorbed molecules clustered on the surface of a macroporous (>50 nm) or non-porous solid at their most favourable site and the absorbent-absorbate interactions are weak (Thommes et al., 2015).

Type III isotherm is characterized by weak gas-solid interactions. It is always observed as not being a very porous material. Therefore, the gas uptake at lower pressure is insignificant. The weak interaction between adsorbent and adsorbate exhibited by the Type III as for the loop observed between the adsorption and desorption branches of the isotherms of calcined catalysts, the hysteresis loop is of Type H1, based on BDDT/BET classification. This type of loop specifies that the material is agglomerated or condensed spheroidal particles of equally constant size and arrangement.

Table 4.6

Surface area, pore volume and pore size of deoiled SBC and doped metal

Catalysts	**Parameters**		
	Surface area (m^2g^{-1})	**Pore volume (cm^3g^{-1})**	**Pore size (Å)**
Deoiled SBC	24.3200	0.132820	218.4544
K-DSBC	8.0127	0.004616	23.0439
Ca-DSBC	10.3493	0.002869	32.2553
La-DSBC	8.1328	0.003739	25.0667

4.2.4 FTIR Analysis of the Catalysts

FTIR analysis is used to obtain the functional groups with the molecules characteristic absorption of infrared radiation and to measure how well a sample absorbs light at certain wavelengths. The FTIR spectra of deoiled SBC, K-DSBC, Ca-DSBC and La-DSBC given in Figure 4.3 which show the presence OH stretching and bending bands are visible at 3250 and 3430 cm^{-1} from H_2O molecules (Lin et al., 1995). There is a shifted from DSBC to the metal impregnated DSBC because of the interaction between metal and OH vibrational effect (Yao et al., 2012). It is further confirmed by bending of OH^- at 486 cm^{-1} (Chin et al., 2009). Yin et al. (2008) has reported, the presence of this band is due to water adsorbed on surface of the catalyst. A band at 1637 cm^{-1} may be due to the presence of basic carbonates generated by adsorption of gaseous CO_2 from ambient atmosphere onto K_2O (Barbosa et al., 2000) and presence of asymmetric stretch, out-of plane bend and in-plane bend vibration modes for CO_3^{2-} molecules. This band can be assigned to stretching vibrations of O-C-O (Granados et al., 2007).

The band at 1050 cm^{-1} is attributed to the alternating Si-O-Si, SiO and Al-O bond (Binitha and Sugunan, 2006). The metal-O-H bending vibration is observable at 486 cm^{-1} for the catalyst. There is no peak observed at 2000 - 2500 cm^{-1} which indicates that no or less organic compound in the sample (Meziti and Boukerroui, 2011).

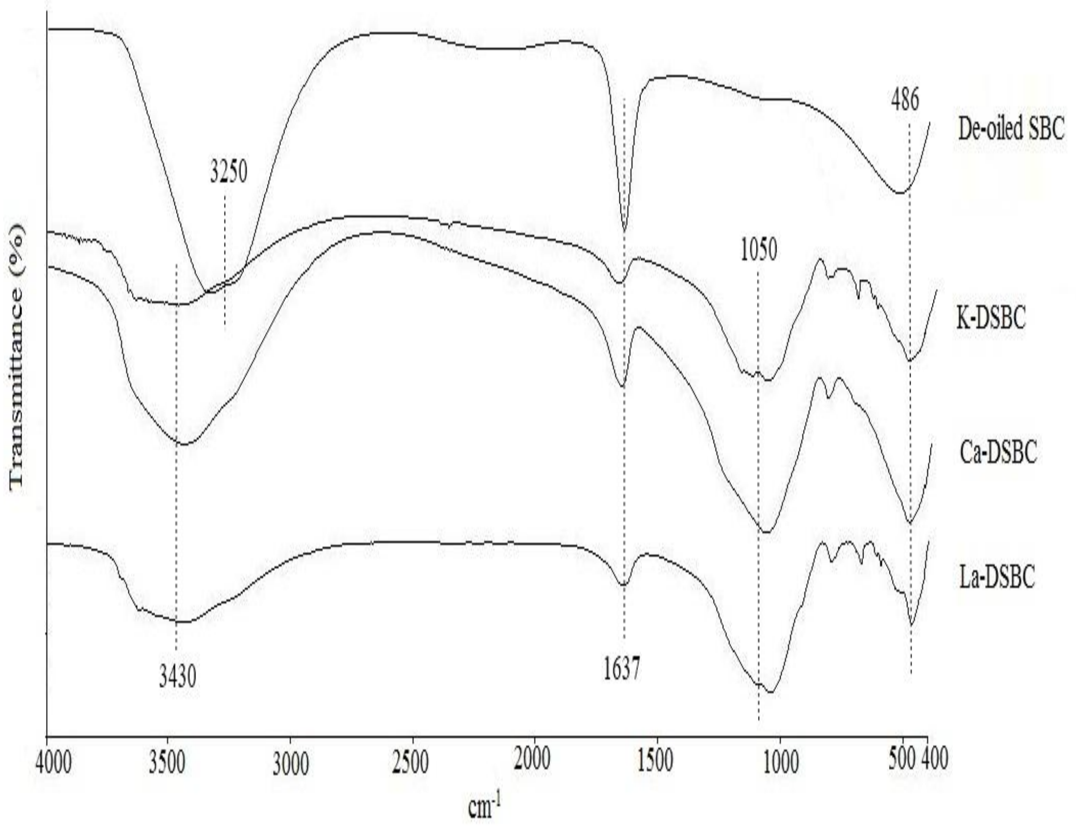


Figure 4.3 FTIR spectra for D-SBC, K-DSBC, Ca-DSBC and La-DSBC.

4.2.5 FE-SEM and EDX Analysis

The FE-SEM micrograph of DSBC exhibited a spongy and porous material. It can be seen from the Figure 4.4, the DSBC exhibited bulk morphologies without clear or defined shape. In contrast, the calcined catalyst at 500 ℃, where morphologies of the catalyst relatively is smaller particles with visible pores of defined shape and size which is spherical.

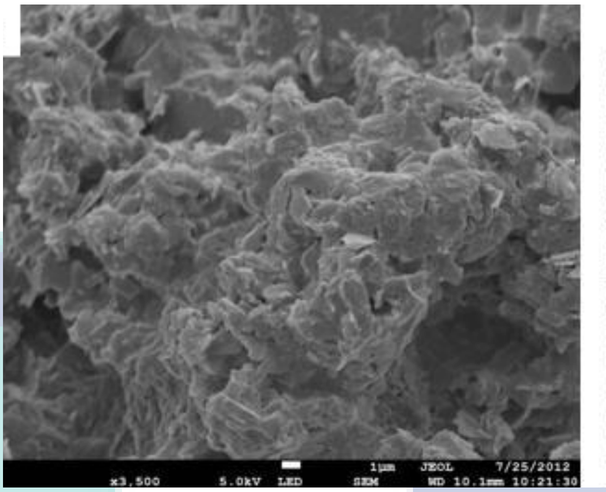


Figure 4.4 FE-SEM image of DSBC.

Morphology of the catalyst is obtained using FESEM and the images were captured under a range of magnifications in order to obtain better image as shown in Figure 4.5. The FESEM image clearly shows that the K, Ca and La were distributed on the surface of the support which is D-SBC by comparing with before and after doped with metal. The K, Ca and La species are spherical in shape and attached on the catalyst support as this is proved by the EDX. The irregular shape of the catalyst indicated its high specific surface area. The impregnation of the K, Ca and La on D-SBC gives basic properties for the catalyst to enable transesterification to be carried out.

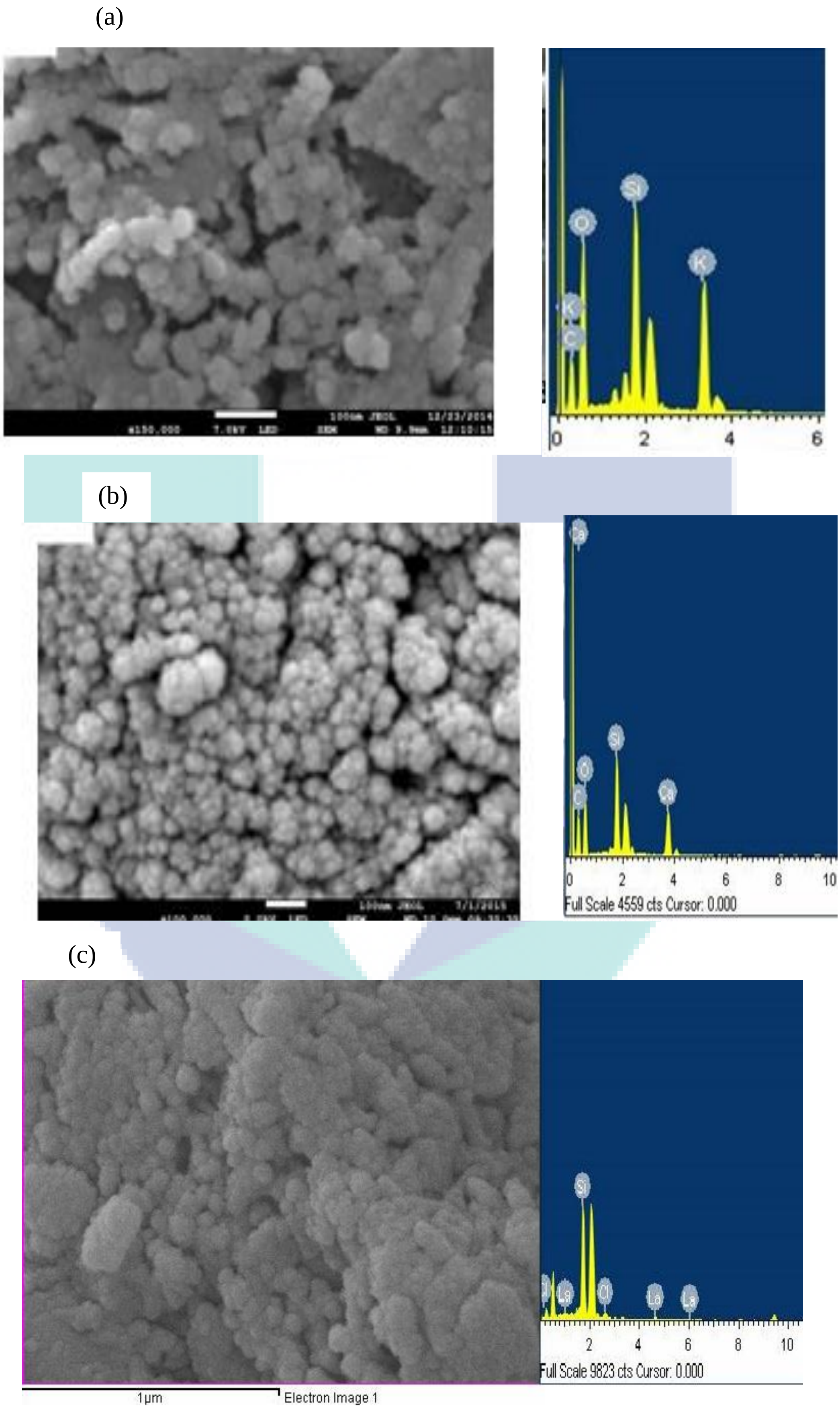


Figure 4.5 FE-SEM and EDX image of (a) K-DSBC, (b) Ca-DSBC and (c) La-DSBC

EDX results in the Table 4.7 shows the corresponding amount of metals in the catalyst of K-DSBC, Ca-DSBC and La-DSBC. Previous studies have also given similar ratio with this argument (Kesić et al., 2012). Based on the EDX, atomic weight of K is 37.30% while Ca is 42.48% and La is 35.47%. The XRF results in Section 4.2.6 reveal the composition as well.

Table 4.7

EDX Analysis for K-DSBC, Ca-DSBC and La-DSBC

Catalyst	Element	Weight (%)	Atomic (%)
DSBC	C	8.16	7.50
	Si	76.72	88.96
	O	15.12	3.54
K-DSBC	C	14.53	5.85
	K	37.30	36.73
	Si	40.42	53.02
	O	7.75	4.40
Ca-DSBC	C	14.03	5.85
	Ca	42.48	44.33
	Si	30.12	41.87
	O	13.38	7.95
La-DSBC	C	8.65	18.68
	La	35.47	13.46
	Si	51.90	60.48
	O	3.98	7.38

Summarized the result from FE-SEM and EDX, conclusion can made that K^+, Ca^{2+} and La^{3+} species were successfully impregnated on D-SBC.

4.2.6 XRF Analysis of the Catalysts

The composition of K-DSBC was investigated using XRF analysis tabulated in Table 4.8. This catalyst was prepared with 40 wt% metal loading onto DSBC. This could be proved by the XRF result where the compositions of metal species of K, Ca abd La were nearly 40 wt%. In line agreement by explanation of XRD pattern (section 4.2.2), element contained in K-DSBC was similar. It consists mainly of K_2O (37.04 %), SiO_2 (29.84 %), Fe_2O_3 (17.29 %) and other oxide is reported in Table 4.7. The mixture of metal oxide greatly contributes to the basicity of K-DSBC in this present study, as observed in basicity analysis by Hammett indicator (section 4.2.7) where it has higher basicity is promised as a pseudo-heterogeneous catalyst for transesterification process, was reported by previous researchers (Chin et al., 2009; Boey et al., 2011b, and Yakoob et al., 2012). K-DSBC was calcined at temperature 500 ℃ and proved that mainly consist of potassium. Ca-DSBC and La-DSBC consist 39.77 % of CaO and 34.82 % of La_2O_3 (This observation is in line agreement with the XRD pattern results (section 4.2.2). SiO_2 content in La-DSBC is 34.82 %, followed by Fe_2O_3 (12.55 %) and other oxides thus made up total of 100.0 %.

The result from Table 4.8 indicates that high amount of calcium (Ca) with 39.77 % total amount from overall content. Since the catalyst was prepared from calcium oxide, the calcium content was high. Meanwhile, the silicon (Si) amount of 34.70 % total from overall content shows the second highest since catalyst is supported by deoiled-spent bleaching clay that is rich in silicon dioxide followed by iron (Fe) and aluminium (Al) with 11.60 % and 8.50 % respectively.

Table 4.8

XRF results of waste catalysts from different metals

Catalyst	**Composition (wt.%)**							**Total**
	K_2O	**CaO**	**SiO_2**	**La_2O_3**	**Fe_2O_3**	**Al_2O_3**	**Others^a**	
DSBC	1.30	1.75	60.40	-	9.31	11.50	15.76	100.00
K-DSBC	37.04	-	29.84	-	17.29	12.18	3.65	100.00
Ca-DSBC	-	39.77	34.70	-	11.60	8.50	5.43	100.00
La-DSBC	-	-	38.55	34.82	12.55	9.46	4.62	100.00

^{a}Others include SO_3, MgO, P_2O_5, TiO_2

4.2.7 Basicity Analysis of the Catalysts using Hammett Indicators

The Hammett indicator test for all of the waste catalysts (K-DSBC, Ca-DSBC and La-DSBC) is provided in Table 4.9. All of the metal doped onto DSBC catalysts showed changes in both the colour of phenolphthalein (H_= 8.2) from colourless to pink and the colour of 2,4-dinitroaniline (H_= 15) from yellow to mauve. However, the colour of 4-nitroaniline (H_=18.4) remained unchanged. This means that the basic strength of this catalyst in the series of 15 < H_ < 18.4. The calcination does not affect to the strength of the catalyst itself.

On the other hand, different case for D-SBC was observed. It showed positive result to phenolphthalein and negative results to both 2,4-dinitroaniline and 4-nitroaniline. The basic strength of them, by the Hammett scale is between 8.2 and 15.0 (8.2 < H_ < 15.0) which is weak base.

Table 4.9

Basicity of catalyst towards Hammett indicators

Waste Catalysts	**Basicity(mmol/g)**		
	Phenolphthalein[a] **H_= 8.2**	**2,4 dinitroaniline[b]** **H_= 15.0**	**4-nitroaniline[c]** **H_= 18.4**
D-SBC	√	X	X
K-DSBC	√	√	X
Ca-DSBC	√	√	X
La-DSBC	√	√	X

Colour change for indicator is [a]colourless to pink, [b]yellow to mauve and [c]yellow to orange) √, colour changed and X, no colour changed

4.3 Transesterification of RBD-PO, WPCO and SBC Oil

For the transesterification reaction carried out with RBD-PO, WPCO and SBC oil, three parameters have been investigated which are influence of catalyst amount, methanol to molar ratio and reaction duration. The transesterification using DSBC itself also had been carried out as depicted in Figure 4.6. It shows that using DSBC alone could not produce good amount since the transesterification reaction produces only 19.2 % of FAME at 5.0 wt%. Hence, we need to doped metal (K, Ca and La) to enhance the transesterification reaction.

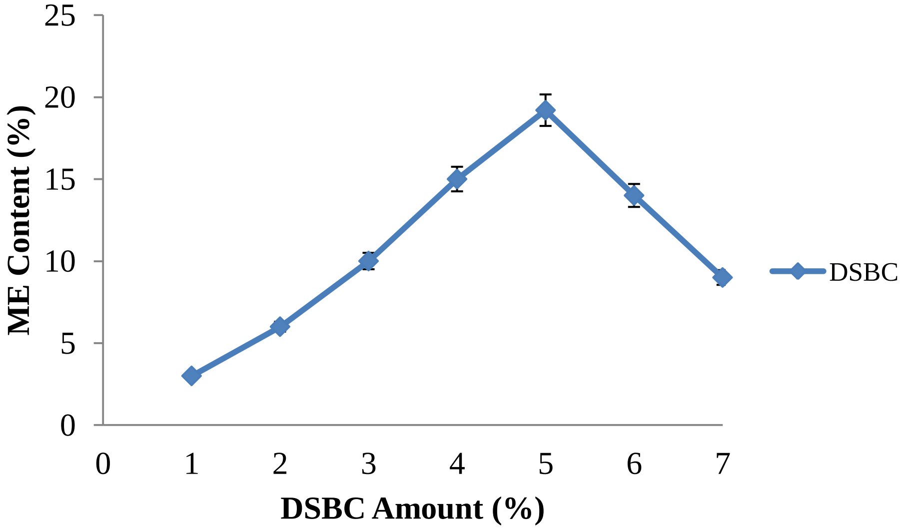


Figure 4.6 Transesterification of DSBC with RBD-PO at MeOH:oil molar ratio 9:1 for 3 h.

4.3.1 Influence of Catalyst Amount in Transesterification

The effect of the catalyst amount (based on oil weight) on transesterification for K-DSBC, Ca-DSBC and La-DSBC are shown in Figure 4.7. In general, the amount of heterogeneous catalyst has a significant positive effect towards the transesterification of vegetable oil to methyl ester due to the number of active sites available for the reaction (Arzamendi et al., 2008). Since oil and methanol are not readily miscible, the temperature, as well as the stirring, are the two important factors that make the two reactants come into contact effectively. The stirring efficiency is also affected at higher catalyst amounts, which probably resulted in much lower methyl esters content. This trend is in agreement with a previous report in which the researcher found that catalyst amounts above 10% leads to stirring complications (Wei et al., 2009). While, Nakatani et al. (2009) reported that increasing the catalyst amount beyond the best value has a negative effect on the purity of the final product.

Figure 4.7 shows that K-DSBC catalyst using RBD-PO and WCO shows that 3% of catalyst presents excellent results (94%). However, the use of SBC oil as feedstock and 5% of catalyst, producing only 88.9% of methyl esters. Thus, the quality of oil used is essential to consider. High quality oil proves that the conversion only needs lesser catalyst amount and aids to the cost effective result. The outcome confirms that the best reaction conditions of transesterification with a constant stirring are able to transesterify RBD-PO and WC oil and SBC oil into biodiesel with the methyl ester conversion. Utilization of DSBC makes the process of preparing biodiesel as a sustainable one. It is also observed that at higher catalyst amount, the ME content decreases as the reaction progresses at longer time.

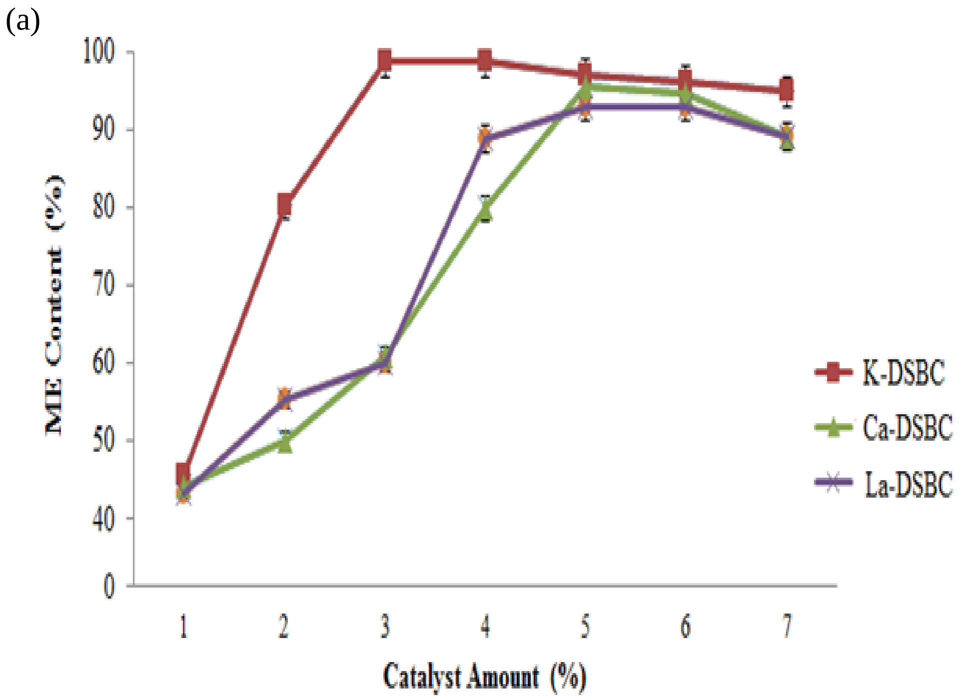


Figure 4.7 Influence of catalyst amount on methyl ester content using (a) RBD-PO (b) WPCO (c) SBC oil at MeOH:oil molar ratio 9:1 for 3 h

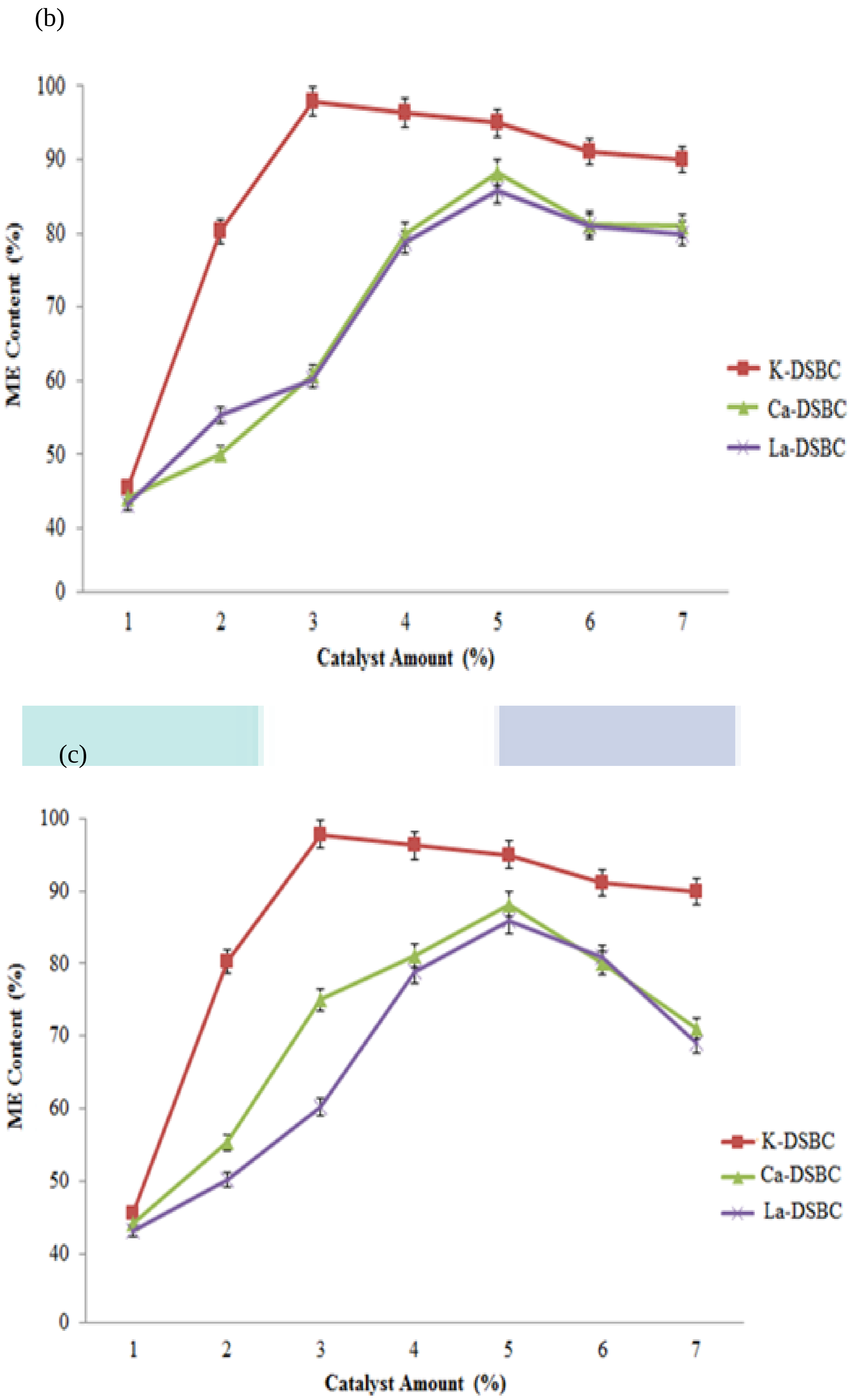


Figure 4.7 continued.

In heterogeneous catalysis, the reaction rate is highly influenced by surface reaction and mass transfer rate. Higher amount of solid catalyst may increase the viscosity of the liquid mixture, therefore increasing the mass transfer resistance (Kim et al., 2004). However, since the reaction mixture constitutes a three phase system, which is oil–methanol-catalyst, there would be diffusion resistance between different phases and affect the reaction rate (Liu et al., 2008). Ideally, when catalyst amount is less, maximum yield cannot be reached. Yet, excessive catalyst amount can also result in saponification reaction. When the catalyst amount is increased from 1 to 5%, the methyl ester content increases (from 78.5% to 88.4%). Further increase in the catalyst amount (beyond 5%) slightly lowers the yields.

According to Meher et al. (2006) high concentrations of alkaline catalyst form soaps in the presence of high free fatty acids, which results in emulsion formation between the soap and water molecules that leads to lowering of yields. In this study, this phenomenon might not be the case, but rather the increase in the amount of catalyst might result in the mixture of catalyst–oil–methanol becomes too viscous giving rise to a problem of mixing and a demand for higher energy for adequate stirring since the SBC oil used is crude with little FFA (~6%). The observation in this study agrees with indicated that increase in triglyceride conversion with an increase in catalyst could occur to some extent and beyond the limitation (Ataya et al., 2008).

The effect of K-DSBC catalyst amount was investigated by varying 1 to 7 wt.%, it was revealed in Figure 4.7 (a). In the illustration shown, the best catalyst amount was achieved at 3% in RBD-PO and WPCO with the maximum yield about 98.9% and 97.8%, respectively. It is because the contact opportunity of the catalyst and the reactant a direct affect to the yield. When the catalyst amount is increased from 3 to 4 wt.%, the yield of the methyl ester decreases, until quiet at 5% and continues to decline at 7 wt.%. It’s probably, when the amount of the catalyst is increased, more products were adsorbed, causing presence of high soap content which will lead to the low activity and furthermore cause methyl esters content decreased. This amount of catalyst used is lower used than previous researches by Boey et al. (2011b) and Chin et al. (2009). The different sources of catalyst and different feedstock give different effects on methyl ester yield.

However, the Ca-DSBC and La-DSBC have achieved 95.6 % and 93.1 % using RBD-PO, respectively. While for WPCO reached of 88.2% and 85.9% of methyl ester with catalyst amount at 5 wt.% and MeOH:oil molar ratio 9:1. Compared of K-DSBC as a catalyst, the catalyst amount of Ca-DSBC and La-DSBC on the methyl ester yield was increased step by step, the best condition was achieved at 5 wt.% of amount catalyst. This is because the low amount of catalyst cannot support the oil yield. The methyl ester yield reaches an best value when the catalyst amount reaches at 5 wt.%, it is due to contact opportunity between the catalyst and the reactant directly affect to the yield. After achieving the best condition point, the methyl ester yield will steadily decrease. The decreasing of methyl ester content at the higher amount of catalyst is due to mass transfer limitation between the solid catalyst and the reactants. It is in agreement, in previous study where the increasing of the catalyst amount beyond the best value has a negative effect on the methyl ester yield (Nakatani et al., 2009; Yang et al., 2009, and Girish et al., 2013).

4.3.2 Influence of Methanol to Oil Molar Ratio in Transesterification

In this research, methanol was chosen as the main variables because of its shortest chain that is suitable to be used as fuel in diesel engines. The longer chain group can also be used in this reaction, but the problem is the reactions will continue until all of the oil has been turned into glycerides and soap instead of esters. Compared to ethanol, methanol gives shorter reaction duration. Georgogianni et al. (2008) found that methanol need shorter time (20 min) compare to ethanol (40 min) to complete the transesterification reaction. The theoretical methanol to oil molar ratio for transesterification is 3:1. However, methanol is not soluble in triglycerides thus producing two phase in the reaction which reduces contraction between two layers. Additionally, the reaction is a reversible reaction. Therefore the excess methanol is needed to carry out the reaction. In this research study, the methanol to oil molar ratio varied from 3:1 to 15:1.

From the Figure 4.8 (a), it can be seen, when the MeOH:oil molar ratio at 3:1 the yield increased rapidly afterward and reached 71.6% and 68.7% using RBD-PO and

WPCO, respectively when catalysed using K-DSBC. Then, it was increased to 99.0% and 98.8% at MeOH:oil molar ratio 9:1. The increasing methyl ester content occurred from 6:1 to 9:1 MeOH:oil molar ratio. However, a drop of methyl ester content was seen after the MeOH:oil molar ratio at 15:1. Further increase of molar ratio did not cause any significant changes in the reaction activity. This may be due to the high ratio is too large and can cause the difficult separation of methyl esters and glycerol as well as complicates the methanol removal process. A similar effect was reported by Meher et al. (2006) and Anwar et al. (2010), where they found high alcohol could increases the solubility of glycerol. Later, it is difficult to separate the glycerol and the forward reaction could to backward equilibrium. Gao et al. (2008) stated that the large amount of methanol addition could dilute the oil and also reduce the reaction rate, resulting in lower yield of methyl ester.

Therefore, the K-DSBC, Ca-DSBC and La-DSBC catalyst reached best MeOH:oil molar ratio at 9:1 where the methyl ester content reached 98.8%, 98.8 and 96.2% using RBD-PO; 97.2%, 85.5% and 83.1% using WPCO; and 88.9%, 80.2% and 76.6%using SBC as referred to Figure 4.8. The use of high MeOH:oil ratios will lead to excess methanol recovery to reduce the cost of production, because any loss in methanol will certainly raise the production cost. In addition, methanol vapour is fire hazard as it is highly flammable.

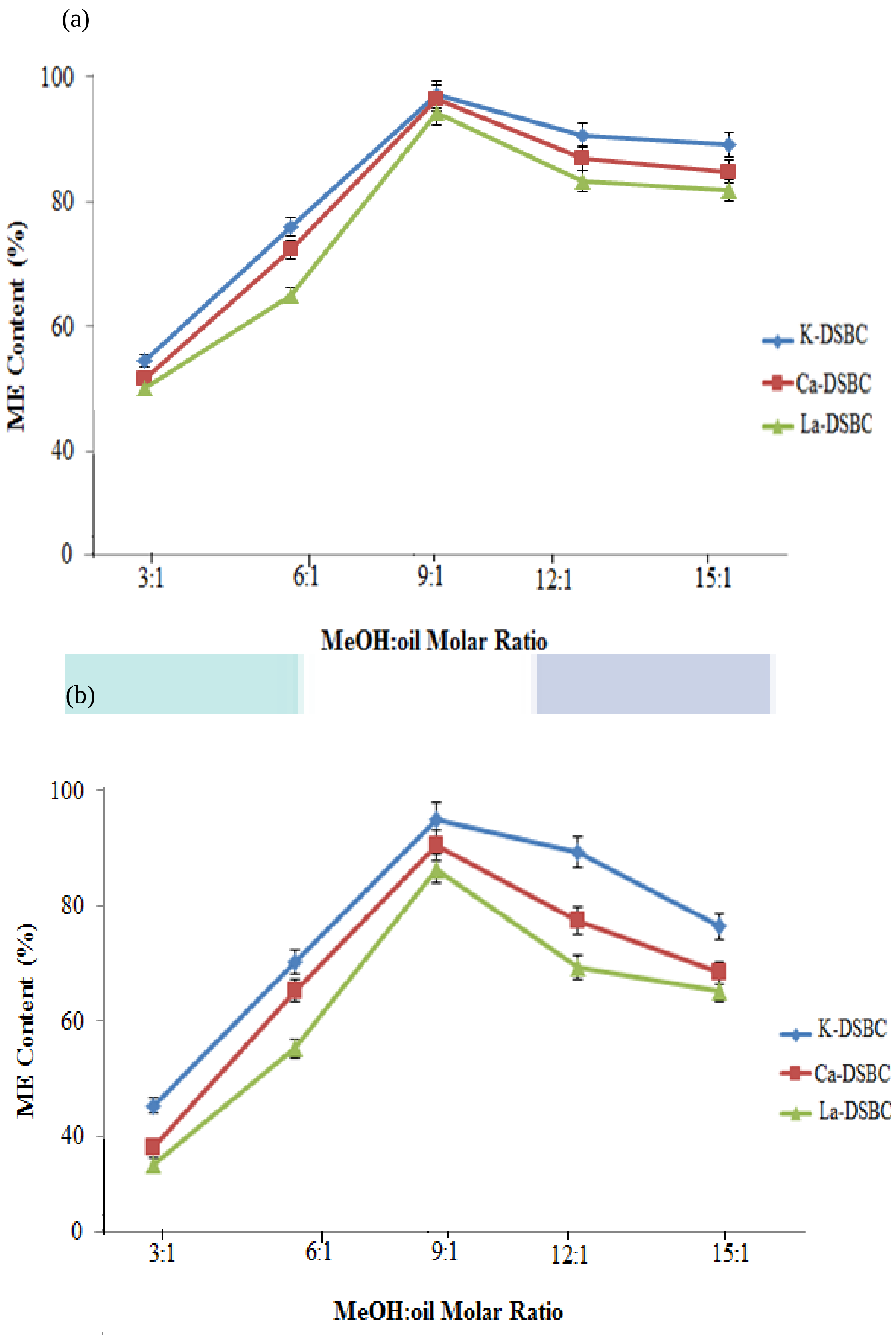


Figure 4.8 Influence of MeOH:oil molar ratio on methyl ester content using (a) RBD-PO (b) WPCO (c) SBC oil at 5 wt.% catalyst for 3 h

(c)

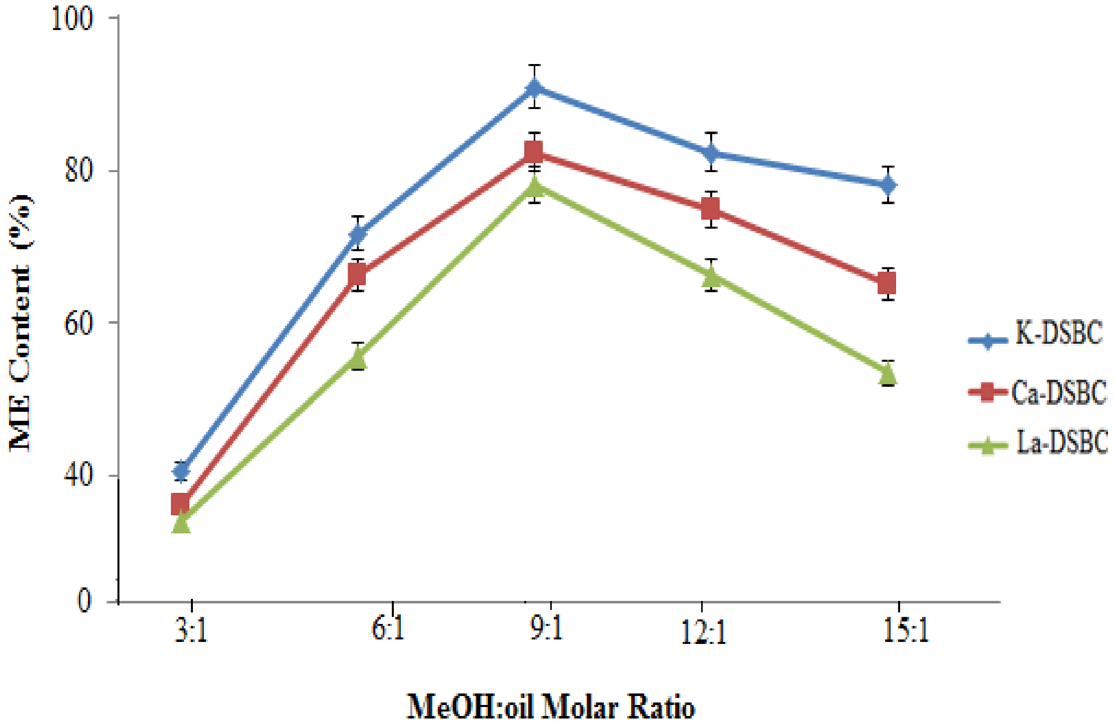


Figure 4.8 continued.

Transesterification of SBC oil using K-DSBC, Ca-DSBC and La-DSBC are conducted under the best condition 5% catalyst amount and 3 h reaction duration. A drastic increase of the ME content is observed from 6:1 to 9:1 MeOH/oil molar ratio compared to steady increase between 3:1 to 6:1. After recording the highest ME at 9:1, the downward trend is observed as much high MeOH/oil molar ratio of 12:1 and 15:1.

However, it is important to note that very high alcohol amounts will add unnecessary cost and complicate the product separation. For higher MeOH/oil molar ratios, excess methanol should be recovered to reduce the cost of production. Usually, industrial scale and pilot plant can recover the methanol. In the small lab scale, it is not possible to recover the excess methanol because the amount is very small. It is possible in many layer scales. Since methanol partitions in the biodiesel/triglyceride phase and the water phase, the methanol in the water phase must be recovered and recycled. If not, the methanol will leave the plant with the waste water, generating an environmental issue as well as growing plant operating costs. Biodiesel and glycerol phase are separated first. Biodiesel contains nearly ~10% (wt.) methanol whereas glycerine contains nearly ~50-60 wt. %. Biodiesel phase is washed with water as it may contain soap and traces of methanol and finally can be dehydrated in rotary evaporator but the amount of the sample must be in a large scale. Another method is using methanol distillation plant where this recovery can be accomplished there. The methanol is distilled in a separate column for recovery.

The suitable amount of methanol (at best level) stimulates the formation of methoxy species on the CaO (K and Ca as well) surface, leading to a shift in the equilibrium in the forward direction, thus increasing the yield rate. Excess methanol helps to promote the reversible reaction forward resulting in a better yield. Practically, a higher molar ratio is required to shift the reaction equilibrium towards the products for more methyl esters. However, increasing the molar ratio may complicate the separation of methyl esters and glycerol as well as complicate the methanol removal process. This causes significant effect to the reaction activity. Too much methanol may cause the dilution effect, thus resulting in fewer yields. It is understood that the glycerol would largely dissolve in excessive methanol and subsequently inhibit the reaction of methanol to the reactants and catalyst, thus interfering with the separation of glycerine, which in turn lowers the yield by shifting the equilibrium in the reverse direction (Gao et al., 2008 and Lim et al., 2009). Since transesterification reaction is a reversible reaction, an excess amount of alcohol (much more than stoichiometry requirement) is always preferred to accelerate the forward reaction.

4.3.3 Influence of Reaction Time in Transesterification

The effect of reaction duration on the transesterification of K-DSBC, Ca-DSBC and La-DSBC are illustrated in Figure 4.9. The figure shows the reaction to transesterify RBD-PO is 2h, meanwhile for WPCO is 3h and for SBC oil is 4h where we can see that lower quality oil need higher reaction time. Transesterification using Ca-DSBC and La-DSBC, gives a lower methyl ester content compared to K-DSBC.

At the beginning of reaction, the progress of the reaction is slow as mixing of oil and methanol is needed in order to increase the concentration. The yield is low during this stage. Afterwards, the reaction proceeds fast and the yield increases until maximum is reached. The yield of FAME remains constant as the equilibrium condition reached (Saba et al., 2016). However, unwanted reactions such as saponification may occur if the reaction time longer than the best reaction time which decrease the yield.

Moreover, it is interesting to note that when the reaction proceeds further the yield decreases, which might be due to the reverse reaction of transesterification, resulting in the loss of esters as well as causing more fatty acids to form soap (Leung et al., 2010). Furthermore, longer reaction duration results in the hydrolysis of esters and causes more fatty acids to form soap (Niju and Anantharaman 2014).

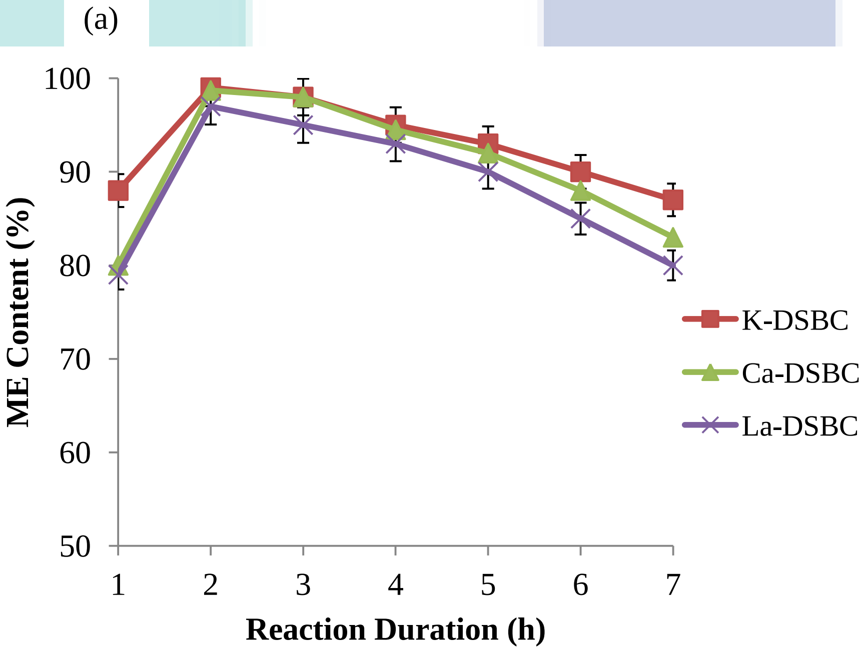


Figure 4.9 Influence of reaction time on methyl ester content using (a) RBD-PO (b) WPCO, (c) SBC-oil (MeOH:oil molar ratio 9:1 at 5% catalyst)

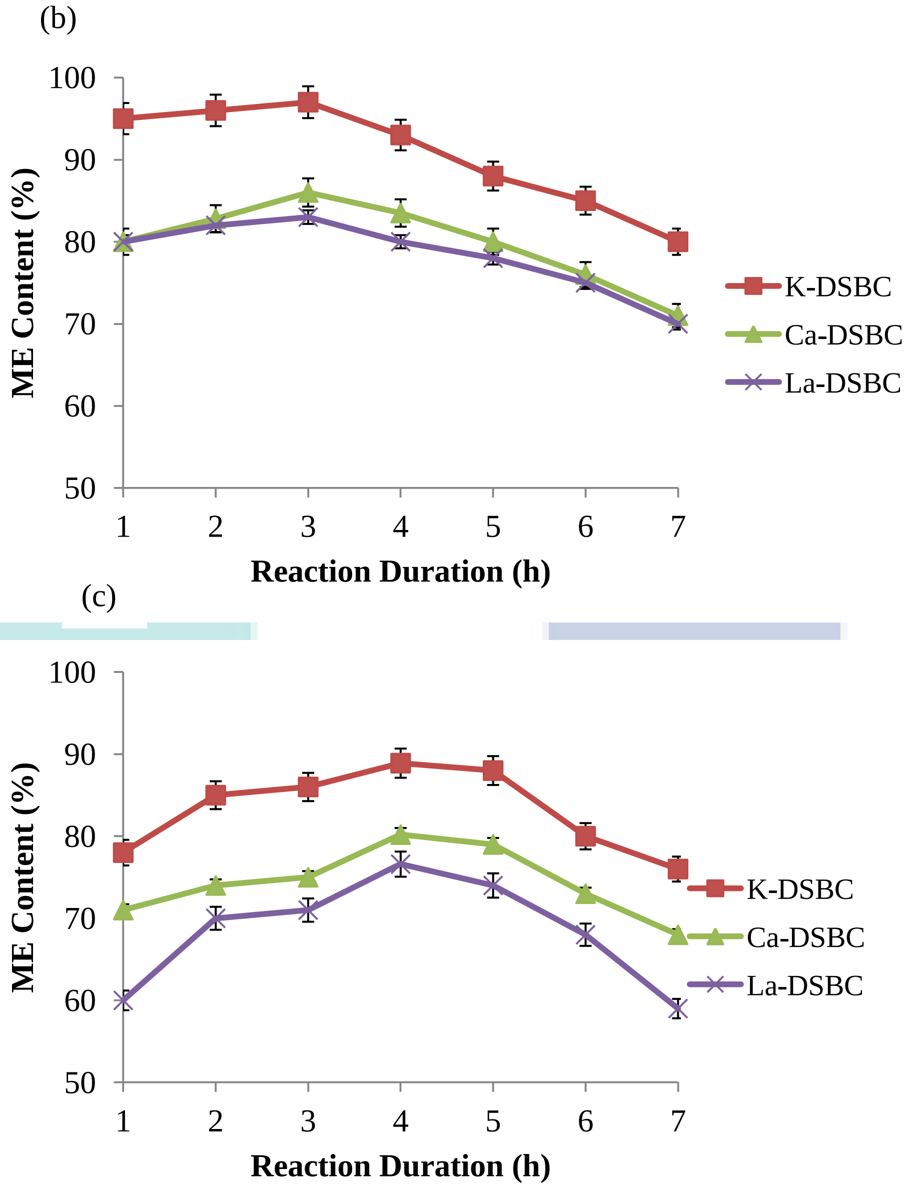


Figure 4.9 continued.

This present study showed that the ME content of SBC reaction catalyzed 88.9% using K-DSBC, 80.2% using Ca-DSBC and 76.6% using La-DSBC in 4 h reaction duration at 65 ± 2 ℃, methanol to oil molar ratio at 9:1 and 5wt.% catalyst as an best reaction conditions.

4.4 Catalyst Activity

In order to study the effect of catalyst activity from the three catalysts (K-DSBC, Ca-DSBC and La-DSBC), experiments using different catalysts were conducted under the best reaction conditions. The reaction time and catalyst amount have influence on catalytic activity of transesterification. From Table 4.10, it can be seen that the lower catalyst amount at 3 wt.% and reaction time of 1 h gave maximum catalytic activity of 0.55 $mol/g_{cat}.s^{-1}$ using K-DSBC catalyst and is comparable with Mahmudul et al. (2017). While for both Ca-DSBC and La-DSBC with catalyst amount of 5 wt.% and reaction time 3 h, the catalytic activity were calculated as 0.11 $mol/g_{cat}.s^{-1}$ using formula in Equation 4.1 below. This is in line with reports of Bond et al. (2006) where the kind of reaction by various types of solid catalysts is determined by the ability of surface to convert the reactants into product. In addition, the activity of the catalyst is defined as the rate of reactant(s) consumption, where the maximum rate will be achieved with combination effects of reactant and the catalyst.

$$\mathrm{TOF} = \frac{\dfrac{n_{\mathrm{mol\ of\ oil}} \times \mathrm{yield\ of\ ME}(\%)}{\mathrm{mol}_{\mathrm{cat}}}}{t} \tag{4.1}$$

Where n is number of mole

mol is number of mole of catalyst

t is reaction duration in h

Table 4.10

Catalytic performances of waste catalysts

Catalyst	ME content (%)	TOF ($mol/g_{cat}.s^{-1}$)
K-DSBC	98.9 ±0.3	0.55 ±0.002
Ca-DSBC	95.6 ±0.4	0.11 ±0.0005
La-DSBC	93.1 ±0.4	0.11 ±0.0003

[a] Reaction conditions: t = 1h, W_{cat} = 3%
[b] Reaction conditions: t = 3h, W_{cat} = 5%

4.5 Reusability, Regeneration and Leaching of Catalysts from Waste Sources

The cost of catalyst commonly affects the overall biodiesel production cost. Reusability is one of the factors in economical application of heterogeneous catalyst. The catalyst was reused without any further activation. After the transesterification reaction, the K-DSBC, Ca-DSBC and La-DSBC catalysts were decanted with simple washing with methanol followed by hexane, for 2 cycles respectively. The aim of washing with methanol is to remove glycerol and for hexane to remove methyl ester and unreacted of triglyceride in the spent catalyst. It is sufficient to clean up the spent catalyst from unwanted compounds. After washing with methanol and hexane, for 2 cycles respectively, the glycerol, triglyceride and methyl ester was removed from spent catalyst.

In order to test the reusability of the catalyst, repeated batch experiments using the transesterification reactions under optimized conditions are applied (reaction temperature of 65 ± 2 ℃, methanol to oil molar ratio of 9:1, catalyst content of 5% and reaction duration of 3 h). Methanol is used to remove the glycerol whereas n-hexane is used to cleanse the residual oil and ME, then dried at 120 ℃ for 2 h, and then calcined at 500 ℃ for 2 h. Figure 4.10 shows the reusability of the synthesized catalyst. This finding highlights the consistent activity up to four runs with a marginal decrease in the FAME yield. The loss of activity suggests that the active sites of the catalyst pores are clogged by large oil molecules, some impurities and contaminants. The degradation of catalytic activity throughout the four runs may be caused by three main reasons: (i) leaching of metal ion from active sites into reaction medium; (ii) harming of the catalyst active sites by the reaction medium (oil, biodiesel and glycerol) which abridged contact amongst basic sites and reactants; (iii) catalyst structure distorted. This study indicates that the activity of regenerated catalyst possesses a good reproducibility (Mahmudul et al., 2017).

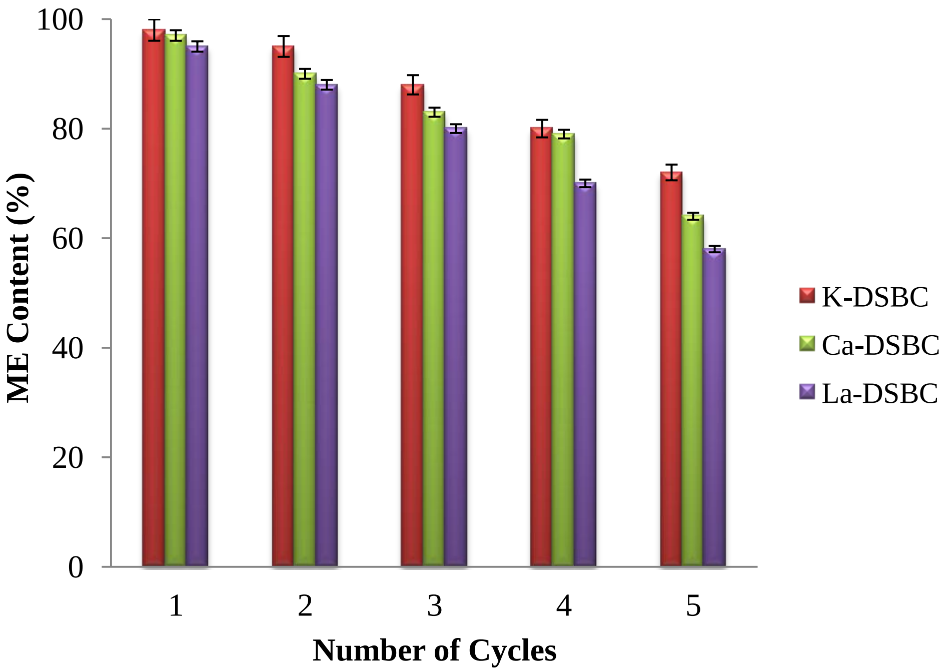


Figure 4.10 The methyl ester content for reuse catalyst of K-DSBC, Ca-DSBC and La-DSBC (condition; catalyst amount of 5%, MeOH/oil molar ratio of 9:1 for 3 h reaction period at 65 ± 2 °C).

The purpose of the leaching study is to determine the stability of solid catalyst as heterogeneous catalyst in transesterification. From the point of view, the leaching of metal to the liquid phase results in the irreversible deactivation of the solid catalysts and it could also lead to the development of activity due to the participation of a homogeneously catalyzed reaction. The main loss of yield in this work is found to be due to leaching of catalyst. The basic oxide could easily form metal hydroxide in methanol thus assisting transesterification of SBC oil without addition of solid catalysts in reaction.

In the case of alkali metals, solubility of alkali metal could be influenced by the atomic size of metal and type of support. Among the heterogeneous base catalysts, CaO is the most studied due to its low price and desired activity. The catalytic activity of CaO strongly depends on calcination temperature and is used since CaO, known to be active in methanolysis reaction (yield over 90% after 90 min (Granados et al., 2007), tends in smaller extent to be leached by methanol (Granados et al., 2009). The alkali earth metal should be supported and the support is usually a porous material providing higher surface area, with catalytic activity ranging from very small to none. One of the properties of support is that it has framework stability, which enables good interaction between active site of support with alkali metal (AlbaRubio et al., 2010; Zabeti et al., 2010 and Albuquerque et al., 2008).

This study demonstrates the very low ME content (10%) is observed by using K-DSBC and Ca-DSBC. The observation proves that it has low leachability to methanol during reaction as referred to Table 4.10. The metal ion leaching into solution or the contribution of the homogeneous reaction due to soluble species created by the dissolution of the solid in methanol is always a primary concern directly affecting catalyst deactivation characteristics. The most interesting case in this study is very small leaching has occurred for La-DSBC as catalyst. This support material (deoiled SBC) is a significant constriction for the use of these basic materials as leaching of the active phase in the reaction medium. It would be forced to introduce additional stages of neutralization and elimination of these species. Yet, in elemental analysis of the normal catalysts, treated catalysts and leachate are investigated using ICP-MS. The observation shows the larger metal content in normal catalyst and treated catalysts as compared to leachate.

Table 4.11

Leaching of the elements from the catalysts analyzed by ICP-MS

Types of element	**Composition (%)**
Potassium	5.8
Calcium	6.5
Lanthanum	4.3

Transesterification of WPCO using spent K-DSBC, Ca-DSBC and La-DSBC under the best conditions are depicted in Figure 4.11. It is found that there is no any significant different between the three catalysts. The catalyst is stable up to second reusable (R_2). For the third reuse (R_3), about 10% of yield decrease is observed and a steady decreases then after. This shows that there is catalyst leaching at third cycle onwards. The decrease in weight of catalyst from first to five cycles is due to the leaching of potassium, calcium and lanthanum mass loses during washing and transferring processes. In a reaction using treated methanol and without catalyst, 63% of methyl ester is produced after 1 h of reaction. This observation confirmed that there is catalyst leaching and the catalyst act as heterogeneous catalysts, in agreement with 87% yield reported for similar reaction by Alonso et al. (2007). The authors found that there was a significant drop in potassium content from 8.16. wt.% to 2.79. wt.% from first to second runs, determined by ICP-AES.

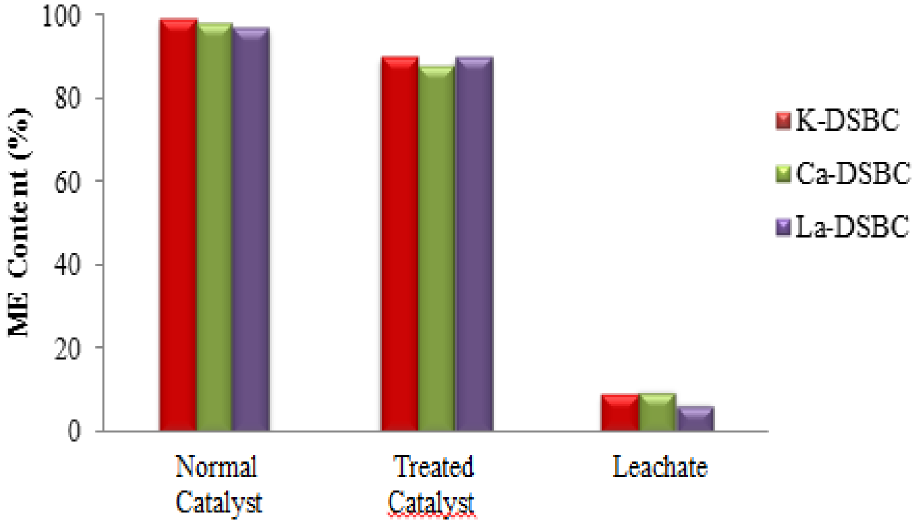


Figure 4.11 Catalyst leachability towards ME content (conditions; catalyst amount 5%; methanol to oil molar ratio 9:1 for 3h reaction duration at 65 ± 2 ℃).

4.6 Tolerance of Waste Catalysts Towards FFA in WPCO

Effects of FFA on transesterification of WPCO (acid value = 3.45 mgKOH/g) to methyl ester using K-DSBC, Ca-DSBC and La-DSBC catalyst are shown in Figure 4.12. In this study, oleic acid was used to modify the FFA content. Figure 4.12 revealed that the effect FFA up to 2.5% level has very significant effect on methyl ester content. The methyl ester content dropped 20% after 2.5% and the content continuous to decrease drastically as FFA content is increased. Much more drastic decrease in methyl ester content (to 5 wt.%) for transesterification using 5 and 7 wt.% In agreement with what was reported by Yan et al. (2009), the higher addition of catalysts could tolerate FFA content compared lower use of catalyst amount. This is because the higher catalyst concentration leads to the presence of relatively more active surface site. These sites make way for reactants to be adsorbed onto and perform the transesterification reaction. At this point the FFA has reacted with the catalyst to form soap and water almost immediately. Soap formation complicates the mixing and product separation processes, meanwhile water accelerates formation of FFA from the remaining triglycerides. Similar observation was observed by (Guo et al. (2010) in which calcined sodium silicate exhibits stable tolerance to FFA when the FFA content is below 2.5% of soybean oil.

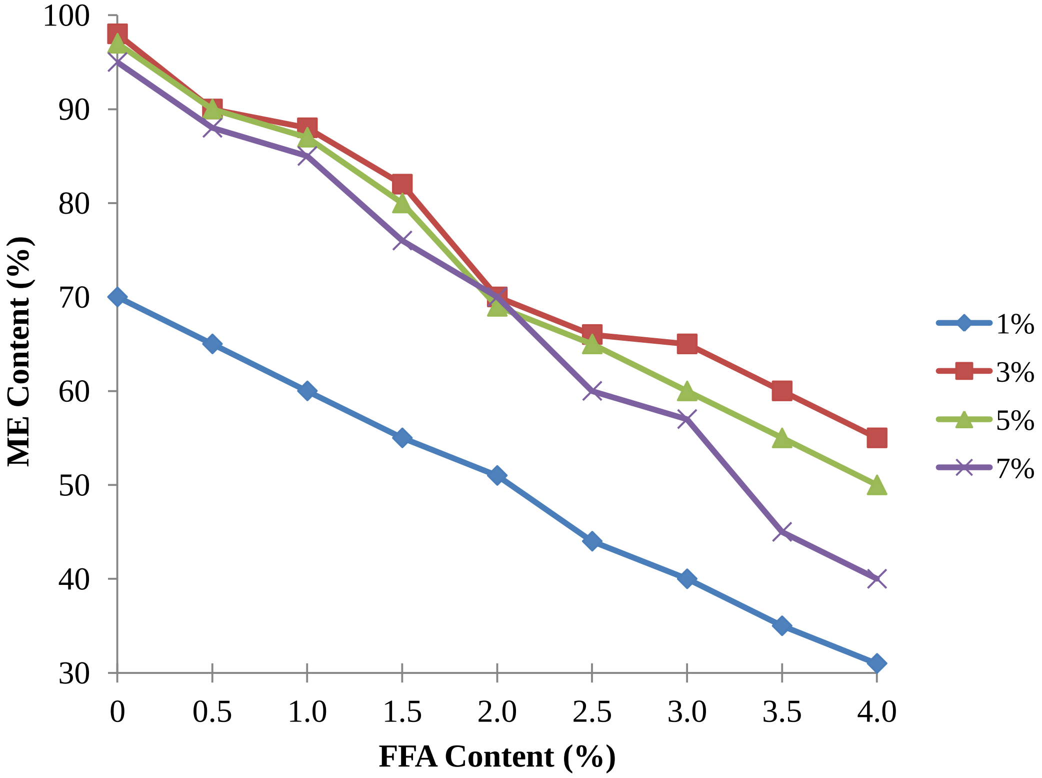


Figure 4.12 Methyl ester content using different catalyst amount with various FFA content (condition; MeOH/oil molar ratio of 9:1 for 3 h reaction period at 65 ± 2 ℃).

Another challenge to increase the catalyst resistance towards the presence of FFA is by looking at increasing the amount of methanol in the reaction system.

Therefore, experiments with varying methanol to oil mass ratios (6:1 to 15:1) are performed at 3 wt.% catalyst amount and the results are presented in Figure 4.13. A catalyst amount of 3 wt.% is chosen as it shows the best performance. It can be seen from the overall results that the excess methanol has not significantly elevated the FFA-resistance of the catalyst, MeOH to oil molar ratios of 9:1 and 12:1 have demonstrated better performance than that of 6:1 and 15:1 at 2.5% FFA. However, when oleic acid is further added (up to 3%), the ME content decreases drastically till 4%.

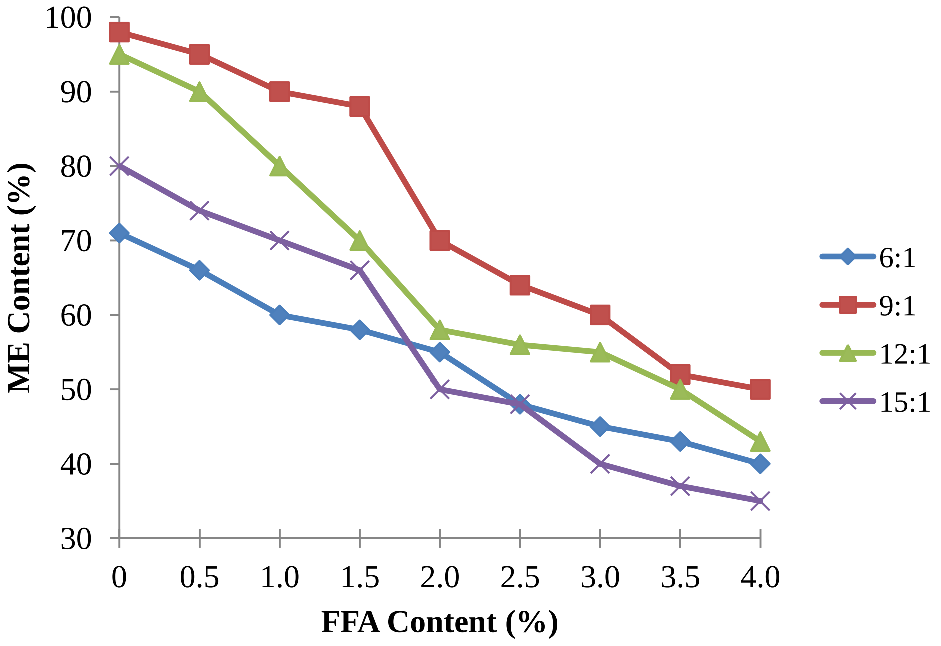


Figure 4.13 Methyl ester content using different MeOH:oil molar ratio with various FFA content (condition; catalyst amount of 3 wt%, for 3 h reaction period at 65 ±2 ℃).

The addition too much of oleic acid into the reaction was decreased of methyl ester content. It is due to reacted of oleic acid with calcium oxide to form calcium oleate and lead soap in the reaction, the mechanism was given in Figure 4.14. In aqueous solution, calcium oleate anion that has sufficient hydrophilicity (through the carboxylate) as well as lipophilicity (through the carbon chain) to act as an emulsifier.

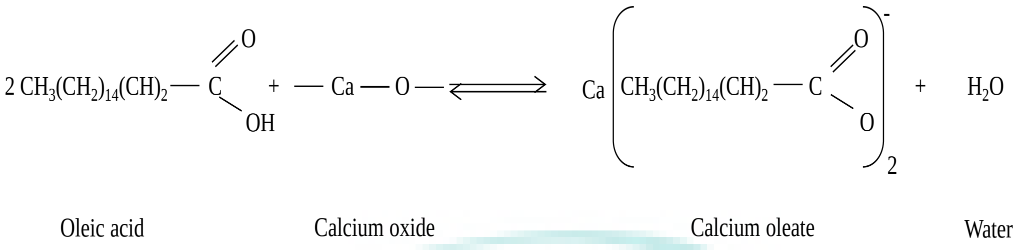


Figure 4.14 Saponification reaction of oleic acid.

4.7 TOLERANCE OF CATALYSTS FROM WASTE SOURCES TOWARDS MOISTURE CONTENT IN WPCO

Effect of water addition using WPCO (moisture content = 0.11%) in transesterification process was studied. The presence of water content with addition 0 wt.%-4 wt.% using K-DSBC, Ca-DSBC and La-DSBC as a catalyst and WPCO as a feedstock with different catalyst amount was presented in Figure 4.15. However presence of water content in transesterification reaction lowered the methyl ester in all variation of catalyst amount as showed in Figure 4.16. The reaction is stable up to 1.0% of water. However, above 1.5% addition of water, there is s a sharp drop in methyl esters content. The tolerance of catalyst towards the presence of water, to a certain extent, is due to the existence of an additional route for the generation of the methoxide ion. The increasing water content in the reaction will decrease the methyl ester content steadily for all variations catalyst amount. The presence of little amount of water in reaction system can enhance the catalytic activity of calcium oxide (CaO) and increase biodiesel yield. It is because of the presence of water; the catalyst surface O2- abstracts H+ from water molecules to form OH- on the catalyst surface. Subsequently, the surface OH- extracts H+ from the hydroxyl group of methanol. This leads to the formation of a methoxide ion, with high activity in the reaction (Atadashi et al., 2012)

In order to achieve the minimal ME content of 90%, water content should be less than 2% (moisture content in the feedstock is 0.28% + adding 1.5%). The presence of too much water could also hydrolyze triglycerides and methyl esters into FFA and glycerol. The 1.0% water tolerance of catalyst is a significant improvement as compared to the homogeneous-catalyzed transesterification. As reported by Boz et al. (2009), the transesterification reaction using base catalyzed required the water content to be less than 0.06%. In line with Canakci and Gerpen, (2001) were the presences of water as little as 0.1% during transesterification reaction will reduce the formation of fatty acid alkyl esters. However, ME continues to decrease drastically as water content is increased. Water creates negative effects, since the presence of water causes formation of soap, consumes the catalyst, reduces its catalytic effectiveness, and results in lower yield (Fadhil et al., 2016).

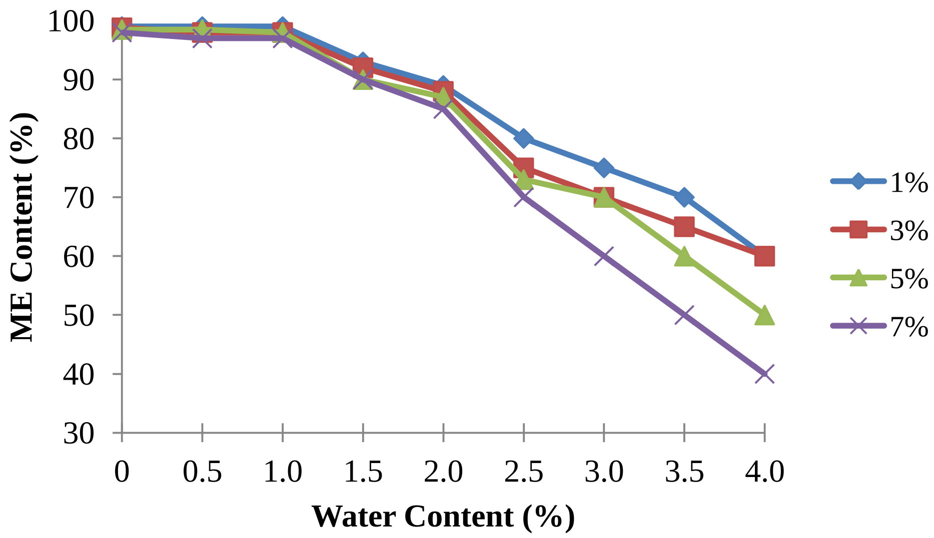


Figure 4.15 Methyl ester content using different catalyst amount with various water content (condition; MeOH/oil molar ratio of 9:1 for 3 h reaction period at 65 ± 2 °C).

Another attempt to increase the catalyst resistance towards the presence of water is by looking at the increasing amount of methanol in the reaction system. Therefore, experiments with varying methanol to oil molar ratios (6:1 to 15:1) are performed at 3 wt.% catalyst amount. Catalyst amount of 3 wt.% is chosen as it shows the best results.

Excess methanol was used to study the catalyst's tolerance towards water, and the results are present in Figure 4.16. However, the use of excess methanol did not bring any significant improvement to the water-tolerance property of the catalyst. As seen in Figure 4.16, the increase of MeOH:oil at 12:1 and 15:1 made the catalyst more tolerant towards addition of water compared to MeOH:oil molar ratio 6:1 and 9:1. However, at

1.5 wt.% water content with MeOH:oil molar ratio 12:1 and 15:1, the methyl ester content reached below 80%. It shows that the heterogeneous catalyst has more tolerance to the water in reaction medium compared to homogeneous catalyst. In the utilization of homogeneous catalyst, the existence of water in the reaction medium can cause a reaction between catalyst with oil to form soap and it will decrease the methyl esters content.

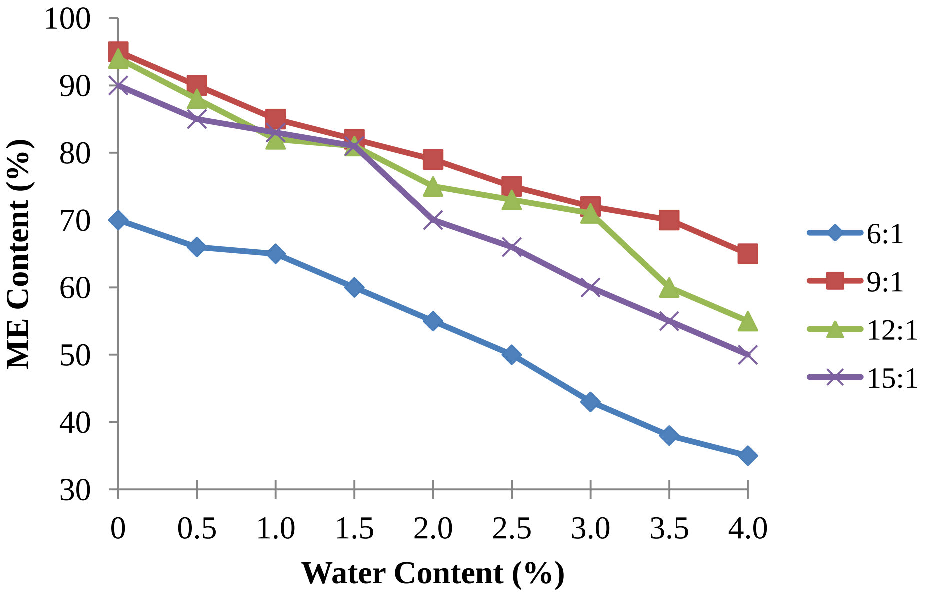


Figure 4.16 Methyl ester content using different MeOH:oil molar ratio with various water content (condition; catalyst amount of 3 wt.%, for 3 h reaction period at 65 ±2 ℃).

The presence of water has a greater negative effect than that of the free fatty acids. So, the water content should be kept below 0.06% (Ma et al., 1998), much lower than the allowable free fatty acids content. These problems may hinder the most efficient utilization of waste vegetable oils and crude oils since they generally contain water and free fatty acids. The present of water in the reaction system could change of the Lewis base site in K-DSBC (metal –O– group) into Bronsted base sites (metal –OH group) (Yan et al., 2009).

4.8 PROPERTIES OF METHYL ESTER

4.8.1 Chemical Properties of Methyl Ester

GC chromatogram proves that methyl ester from transesterification of RBD-PO, WPCO and O-SBC using K-DSBC as a catalyst, shown in Figure 4.17. In RBD-PO and WPCO mainly consists of methyl ester of oleate ((C18:1) 45.2% and 42.3 %), palmitate ((C16:0) 37.0% and 28.2%), linoleate ((C18:2) 12.2 and 18.1%), respectively. The minor constituents such as stearate (C18:0), stearic (C18:3), myristate (C14:0), laurate (C12:0). From the Figure 4.18 shown, the presence of palmitoleate (C16:1) 4.8 % in the chromatogram of WPCO, while not present in RBD-PO, it was explained in section 4.1.1 and the methyl heptadecanoate (C17:0) as an internal standard also shown in all chromatogram. From GC chromatogram methyl ester content was calculated using formula in section 3.7.2 and was found that methyl ester content of RBD-PO and WPCO was achieved 99.0% and 98.8%, respectively. While, for GC chromatogram of methyl ester from transesterification of O-SBC, shows the methyl ester of palmitate (C16:0) 43.9% is the major methyl ester fatty acid followed by oleate (C18:1) 41.6% and linoleate (C18:2) 11.5%. Stearic (C18:3), palmitoleate (C16:1), myristate (C14:0), and laurate (C12:0) are minor constituents. The methyl ester content was calculated of 88.9% using GC analysis.

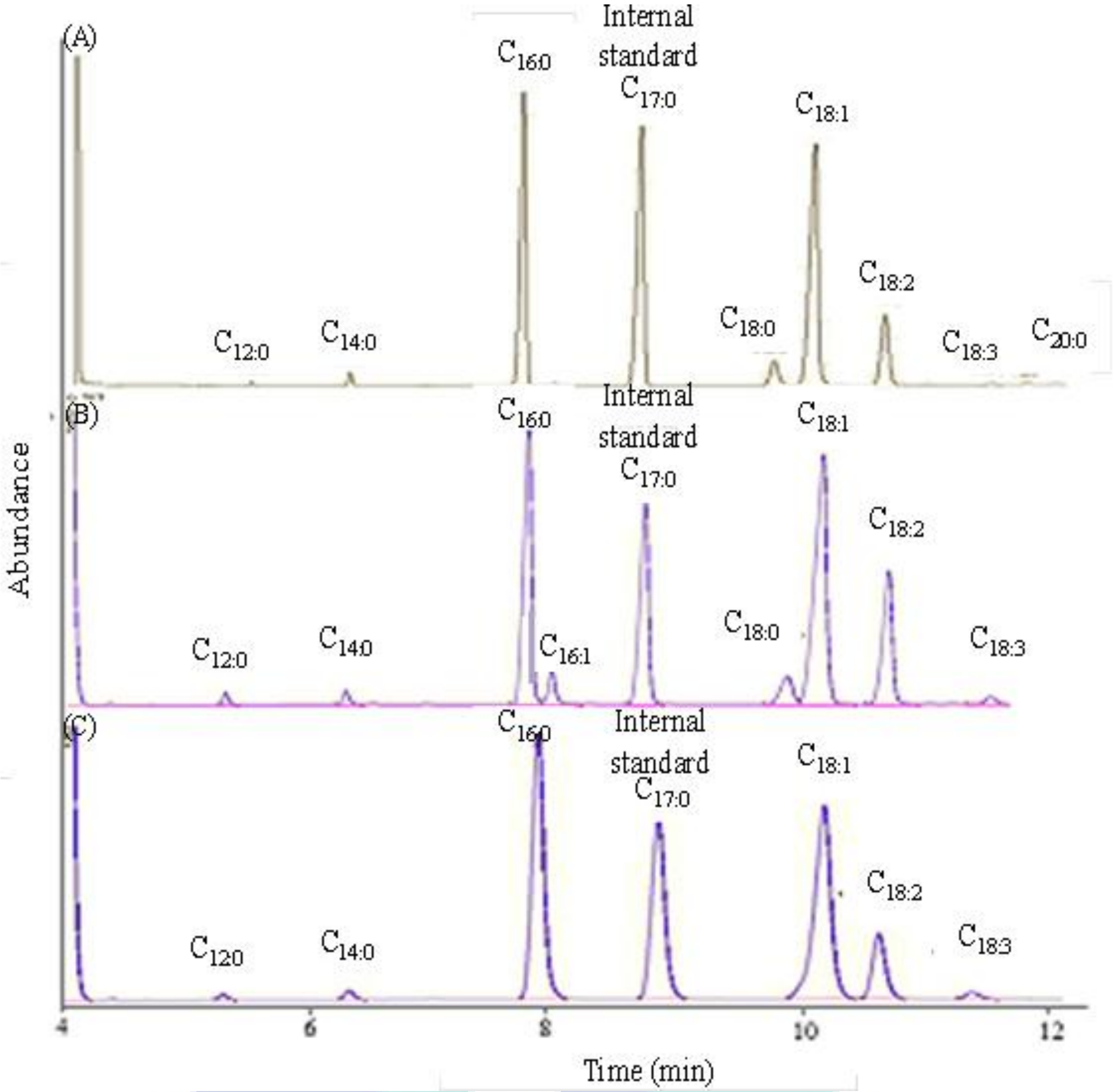


Figure 4.17 Gas chromatogram methyl ester with K-DSBC as a catalyst (A) RBD-PO, (B) WPCO and (C) SBC oil.

For comparison, the integration of methyl ester content from transesterification of RBD-PO, WPCO and O-SBC using ^{1}H NMR was observed, shown in Figure 4.18.

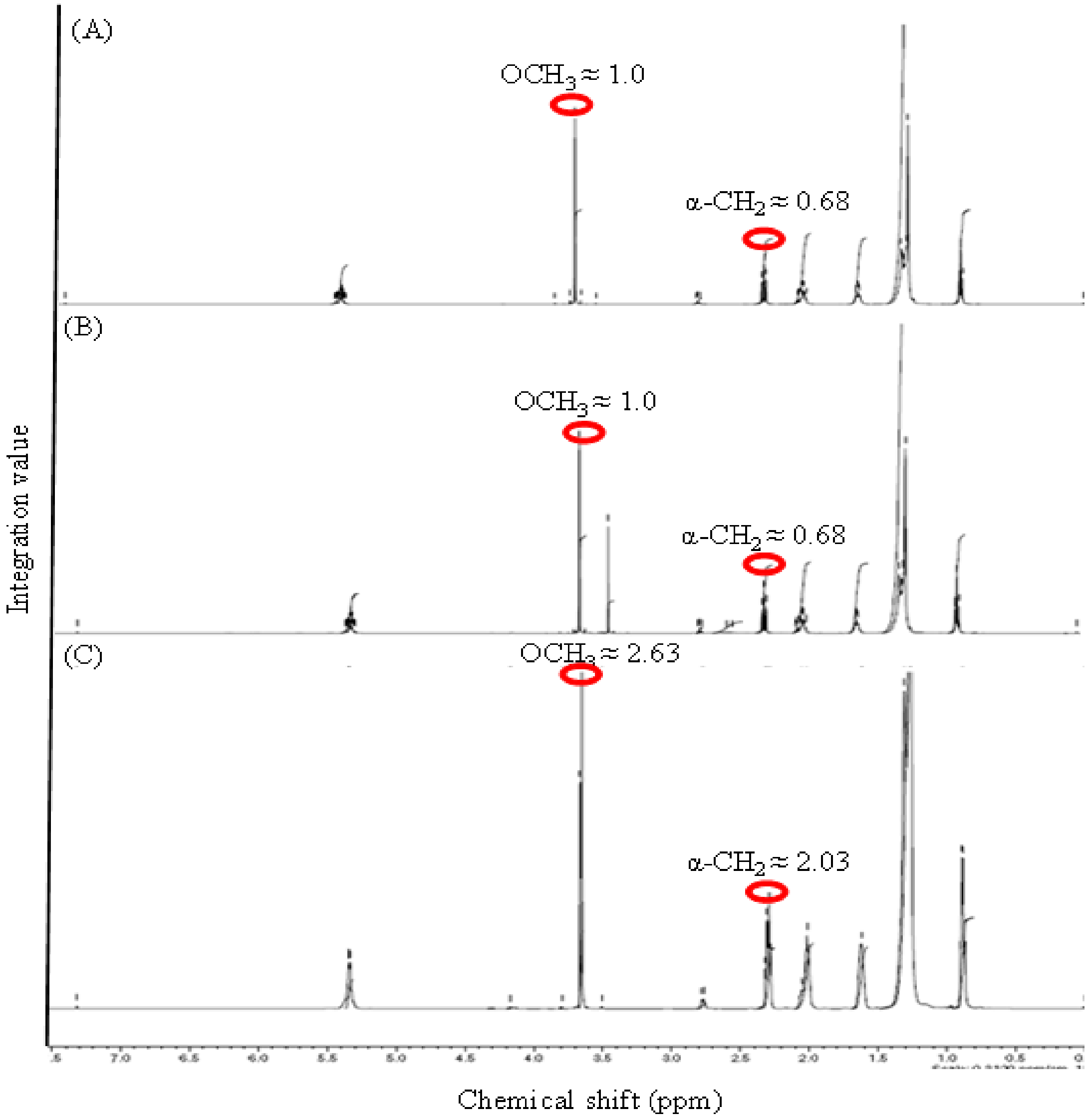


Figure 4.18 ^{1}H NMR spectrum methyl ester with K-DSBC as a catalyst (A) RBD-PO, (B) WPCO and (C) SBC oil.

The ^{1}H NMR spectrum was found A_{ME} appears at 3.7 ppm, while $A_{\alpha\text{-CH2}}$ appears at 2.3 ppm.

4.8.2 Physical Properties of Methyl Ester

Properties of biodiesel from K-DSBC, Ca-DSBC and La-DSBC using RBD-PO as a feedstock are tabulated in Table 4.12. It shows that the ester content of the final products was determined following EN 14103 standard. The density and viscosity of the fuels affect the start of injection, the injection pressure, and the fuel spray characteristic, so that they influence the engine performance, combustion and exhaust emissions. Many performance characteristics such as cetane number and high heating value (HHV) are related to the density. In addition, since the diesel fuel injection systems measure the fuel by volume, the fuel density will influence engine output power due to a different mass of fuel injected (Bahadur et al., 1995). Viscosity is also of among the important properties of methyl ester, as viscosity gives effect to the fuel atomization and engine deposits (Knothe, 2001). By transesterification process, the viscosity can be reduced drastically, so it could be suitable for diesel engine. The biodiesel has flash point greater than petroleum diesel, makes biodiesel as much safer substance than petroleum diesel. The cold point is the temperature, when crystals form in the fuel, the cloud point biodiesel higher than petro diesel. The HHV is one of the important analyses in the production biodiesel, measured using bomb calorimeter. The cold point and HHV is among the physical important parameters in ignition of biodiesel (Ali et al., 2016).

Table 4.12

Properties of the prepared biodiesel with different catalysts

Property	**Method (Specification)**	**K-DSBC**	**Ca-DSBC**	**La-DSBC**	**Unit**
Ester content	EN 14103 (96.5 Min.)	99.0 ± 0.4	98.8 ± 0.4	97.2 ± 0.3	% (m/m)
Density (15 ˚C)	EN ISO 3675 (860 – 900)	882	880	887	kg/m^3
Viscosity (25 ˚C)	EN ISO 3104 (3.5 – 5.0)	4.3	4.2	4.0	cP
Flash Point	ASTM D93 (>130 °C)	156	156	168	˚C
Cloud Point	ASTM D2500 (-)	10	8	8	˚C
HHV	ASTM D240 (35 Min.)	38.0	38.6	39.2	MJ/kg
Sulfur content	D 5453 (0.05 Min.)	0.04	0.045	0.045	% (mass)

Reaction conditions K-DSBC: Catalyst amount, 3 wt.%; MeOH:oil molar ratio, 9:1 for 2 h. Reaction conditions Ca-DSBC and La-DSBC: Catalyst amount, 5 wt.%; MeOH:oil molar ratio, 9:1 for 2 h.

According to the Demirbas (2008), density of biodiesel has values between 848 kg/m^3 to 885 kg/m^3. An increase in density up to 885 kg/m^3 for biodiesel will highly increase the viscosity. The viscosity values of ME decreases sharply after transesterification process (vegetables oils are between 57.2 and 64 cP). The viscosity value in biodiesel is due to the presence of hydroxyl groups to form hydrogen bonding in fatty acid molecule or sometimes ME associated with unreacted triglycerides in the fuel (Okullo et al., 2012). Due to the structural differences in the fatty acids constituent of catfish oil and SBC oil, the properties of both show different results. Palm oil is predominantly made of palmitic acid (C16:0), a saturated fatty acid that is associated with higher energy content than unsaturated acids (Okullo et al., 2012).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The experiments have produced many outcomes that can be concluded as below:

i. The transesterification uses RBD-PO, WPCO and SBC oil with best condition is using K-DSBC catalyst resulting ME content over 98.9% using 3 wt.% catalyst and 9:1 methanol to oil molar ratio. The best reaction period for RBD-PO is 2 h, WPCO is 3 h and SBC oil is 4 h.

ii. All the three catalysts can be reuse up to five cycles, while maintaining methyl esters content above 88%. The tolerance towards FFA and water was studied. K-DSBC and Ca-DSBC could tolerate FFA until 1.25 wt.% and water 1.75 wt.%. While La-DSBC could tolerate FFA until 1.75 wt.% and water 2 wt.%, with ME content over 80% for both catalysts.

Waste source as a feedstock and catalyst are the best options for decreasing the cost of biodiesel production and for this research, waste cooking oil provides the best methyl ester yield with K-DSBC.

5.2 Recommendations

Through the research, it was successfully investigated a series of experiments on transesterification, a number of recommendations are proposed to enhance the whole research as listed below:

i. For the further research work, different catalysts preparation method should be done to investigate their effectiveness in transesterification.

ii. The tolerance study of the catalyst towards a specific saturated and unsaturated fatty acid.

iii. The study on different method of transesterification should be carried out such as sonication and *in-situ* transesterification.

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APPENDIX

List of Publications

1. Oral presentation (2015-2016)

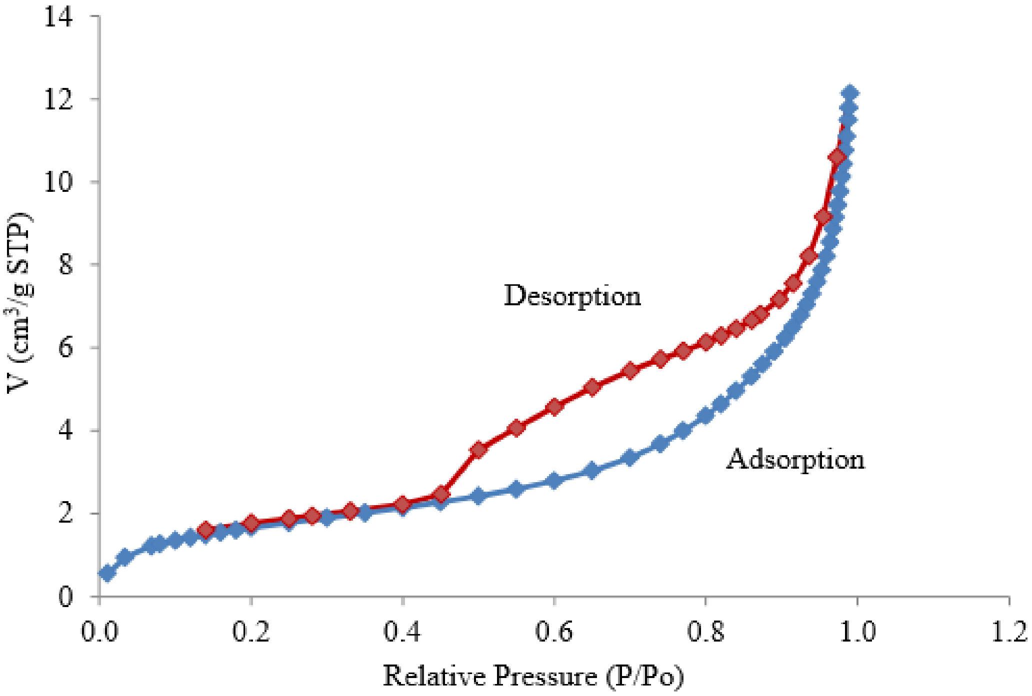
- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim. *Transesterification of waste cooking oil using K/Si/Fe_3O_4 magnetic composite as a solid catalyst.* Presented at the National Conference for Postgraduate Research (NCON-PGR) 2015, 24-25 Januari, 2015, Universiti Malaysia Pahang, Gambang, Pahang, **Malaysia**.
- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim**.** *Utilization of Ca/Si/Fe_3O_4 magnetic composite as a solid catalyst in transesterification of waste cooking oil.* Presented at the Conference on Nano & Bioresource Technology (NBT) 2015, 28-29 March, 2015, Universiti Kebangsaan Malaysia, Bangi, Selangor, **Malaysia**.
- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim. *Utilization of deoiled deoiled spent bleaching clay (SBC) as a catalyst in transesterification of palm olein.* Presented at the Engineering Technology International Conference (ETIC) 2015, 10-11 August, 2015, Wina Holiday Villa, Kuta, Bali, **Indonesia.**
- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim. *Transesterification of waste cooking oil using potassium loaded on deoiled spent bleaching clay (SBC) as a solid base catalyst.* Presented at the International on Fluids and Chemical Engineering (Fluids-CHE) 2015, 25-27 November, 2015, Adya Hotel, Langkawi, Kedah, **Malaysia.**
- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim. *Impregnation of K^+ over deoiled spent bleaching clay (SBC) as a catalyst in transesterification.* Presented at the National Conference for Postgraduate Research (NCON-PGR) 2016, 24-25 September, 2016, Universiti Malaysia Pahang, Pekan, Pahang, **Malaysia**.

2. Exhibition (2016)

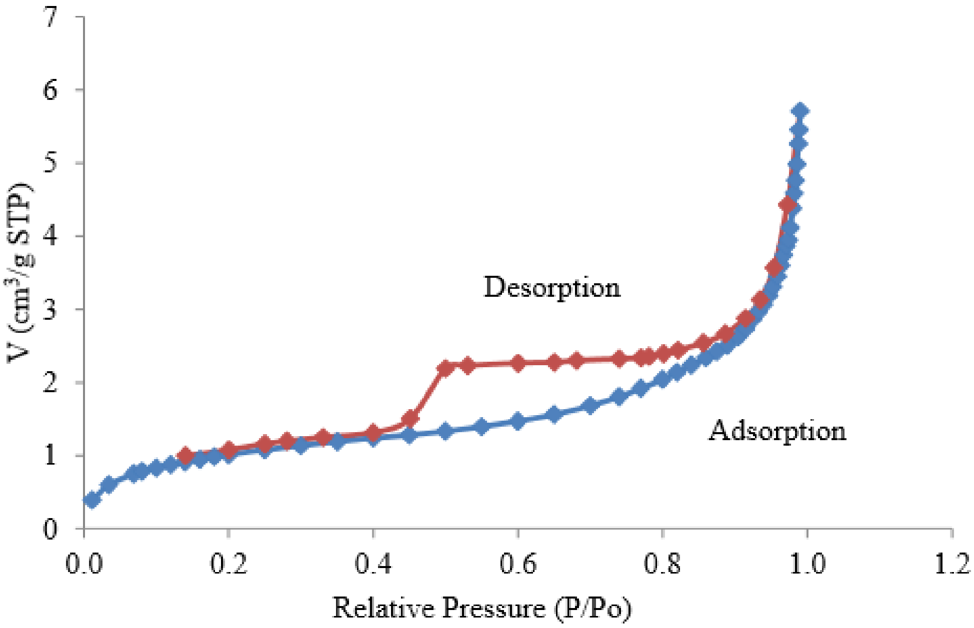
- Sang Ging Yee, Gaanty Pragas Maniam, **Rehan Zainol Abidin,** Nazratul Zaheera Abdul Kapor, Mohd Hasbi Ab. Rahim, Sharmalla Subramaniam. *Utilization of Waste SBC as Feedstock and Catalyst for Greener Fuel.* Presented at (CITReX), 7-8 March, 2016, Universiti Malaysia Pahang (UMP), Gambang, Pahang, Malaysia. (Gold)
- Sang Ging Yee, Gaanty Pragas Maniam, **Rehan Zainol Abidin,** Nazratul Zaheera Abdul Kapor. *Utilization of Waste SBC as Feedstock and Catalyst for Greener Fuel.* Presented at International Festival Innovation on Green Technology (i-FINOG), 15-17 April, 2016, Universiti Malaysia Pahang (UMP), Gambang, Pahang, Malaysia. (Silver)

3. Journal (2016)

- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim. 2016. Utilization of de-oiled spent bleaching clay as a catalyst for transesterification of palm olein. *ARPN Journal of Engineering and Applied Sciences.* **11(11)**: 7309-7312.
- **Rehan Zainol Abidin,** Gaanty Pragas Maniam, Mohd Hasbi Ab. Rahim. 2016. Transesterification of waste cooking oil using calcium loaded on deoiled spent bleaching clay as a solid base catalyst. *Bulletin of Chemical Reaction Engineering and Catalysis.* **11(2)**: 176–181.



N_2 adsorption-desorption isotherm for D-SBC



N_2 adsorption-desorption isotherm for K-DSBC