COMBINATION OF MUSSEL SHELL AND POTASSIUM HYDROXIDE AS SOLID WASTE BASIC CATALYST (SWBC) FOR FATTY ACID METHYL ESTER (FAME) SYNTHESIS FROM CASTOR OIL

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ABSTRACT

Continuous use of fossil fuel can cause decreasing of fossil fuel resources and increase petroleum price. Biodiesel provide a great path in helping human to reduce the dependence on non-renewable petroleum derived fuel. Initially, biodiesel is produced from edible oil feedstock such as palm oil and as the demand for biodiesel ascending, the feedstock for food truncating thus pose a threat to food chain. The main purpose of this research is to synthesis fatty acid methyl ester (FAME) from castor oil. The effects of different catalysts, temperature and reaction time are also studied. Two catalysts were prepared, where mussel shell waste being calcined to produce calcium oxide (CaO) and then the other one CaO impregnated with potassium hydroxide (KOH) to produce *solid waste basic catalyst* (SWBC). The SWBC were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), and Thermal Gravimetric Analysis (TGA). The castor oil was converted into biodiesel through transesterification in a presence of methanol and two different SWBC. CaO/KOH was the best SWBC which yields, 91.17%, the highest biodiesel produced from Castor oil and had a potential to be an alternative low cost catalyst and at the same time improve the yield of FAME.

ABSTRAK

Penggunaan berterusan bahan api fosil boleh menyebabkan berkurangan sumber bahan api fosil dan menaikkan harga petroleum. Biodiesel menyediakan jalan yang besar dalam membantu manusia untuk mengurangkan pergantungan kepada bahan api petroleum yang tidak boleh diperbaharui diperolehi. Pada mulanya, biodiesel dihasilkan daripada bahan mentah minyak yang boleh dimakan seperti minyak kelapa dan kerana permintaan yang meningkat untuk biodiesel, bahan mentah untuk makanan berkurangan itu menimbulkan ancaman kepada rantaian makanan. Tujuan utama kajian ini adalah untuk sintesis lemak asid metil ester (FAME) daripada minyak kastor. Kesan pemangkin yang berbeza, suhu dan masa tindak balas juga dikaji. Dua pemangkin disediakan, di mana sisa kepah shell yang dibakar untuk menghasilkan kalsium oksida (CaO) dan pemangkin yang lain CaO impregnated dengan kalium hidroksida (KOH) untuk menghasilkan pemangkin asas sisa pepejal (SWBC). The SWBC telah dianalisiskan oleh pembelauan sinar-X (XRD), sinar-X pendarfluor (XRF), dan Analisis gravimetrik Thermal (TGA). Minyak kastor telah ditukar kepada biodiesel melalui transesterifikasi dalam kehadiran metanol dan dua SWBC berbeza. CaO / KOH adalah SWBC yang terbaik, di mana 91.17%, biodiesel yang paling tinggi terhasil daripada minyak Castor dan mempunyai potensi untuk menjadi alternatif pemangkin kos rendah dan pada masa yang sama meningkatkan hasil FAME.

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LIST OF ABBREVIATIONS

FAME	Fatty acid methyl ester
SWBC	Solid waste basic catalyst
CaO	Calcium oxide
KOH	Potassium hydroxide
GC-MS	Gas chromatography mass spectrometry
FTIR	Fourier transform infrared spectroscopy
TGA	Thermal gravimetric analysis
XRD	X-ray diffraction
XRF	X-Ray Fluorescence

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1 INTRODUCTION

Majority of the world energy needs are supplied through fossil fuel sources like petroleum, natural gases and coal, with the exception of hydroelectricity and nuclear energy, of all, these sources are dwindling day by day.

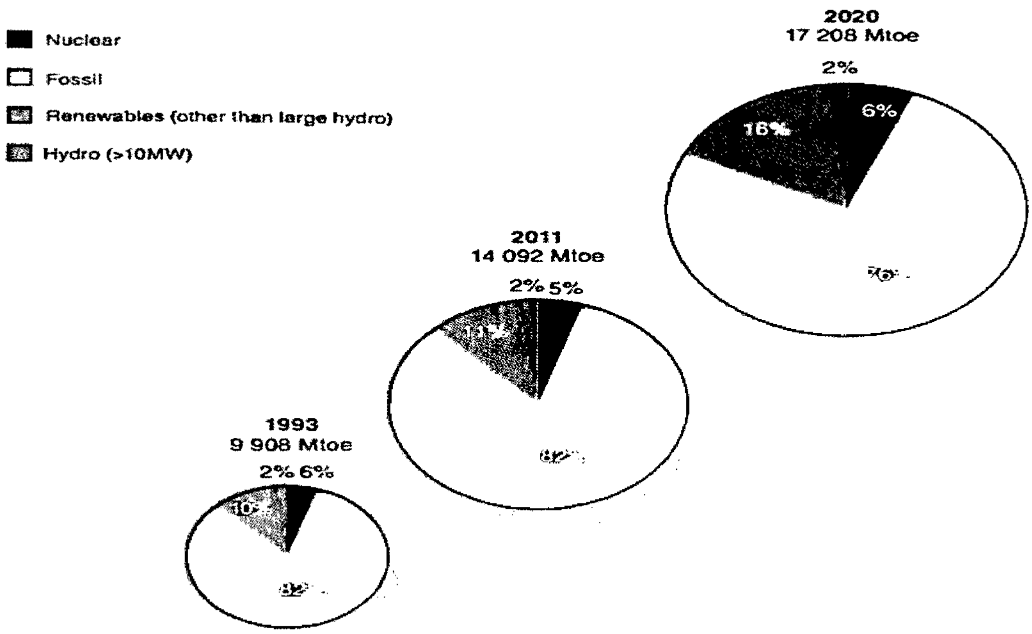
Diesel fuels have an essential function in the industrial economy of developing country and used for transportation and agricultural goods and operation of diesel tractor and pump sets in agricultural sector (Meher et al. 2006).

Table 1.1 Important characteristic of diesel fuels

Fuel characteristics	Comments
Cetane number	A measure of ignition quality of diesel fuels High cetane number implies short ignition delay Higher molecular weight normal alkanes have high cetane numbers
Specific gravity	Required for the conversion o measured volumes to volumes at standard temperature of 15 °C.
Flash point	Indicates the presence of highly volatile and flammable materials Measures the tendency of oil to form a flammable mixture with air Used to access the overall flammability hazard of a material
Viscosity	Proper viscosity of fuel required for proper operation of an engine Important of flow of oil through pipelines, injector nozzles, and orifices.
Ash	Results from oil, water soluble metallic compounds or extraneous solids, dirt and rust

Source: (Srivastava and Prasad 2000)

These sources are few in number and they already reach their peak production. Besides that, increasing emission of pollutant also becomes worst day by day.



Source: WEC Survey of Energy Resources 1995, World Energy Resources 2013 and WEC World Energy Scenarios to 2050 (World Energy Resources, 2013)

Due to these problems, many studies have being headed towards the new way of renewable fuel to save the world future energy crisis. Development of biodiesel is an alternative fuel, environmental friendly, biodegradable and is produced from either edible or non-edible oils (Junaid et al. 2014). Chemically biodiesel is defined as monoalkyl esters of long chain fatty acids derived from reneable feedstock like vegetables oils and animal fats (Meher et al. 2006). There are many ways and procedures to produce biodiesel like blending, micro-emulsion, pyrolysis and transesterification, but transesterification is the most practicable and less

Figure 1-1 Total Primary Energy Supply

expenditure process. The main advantages of using biodiesel are its renewability, better-quality, exhaust gas emission, it does not contribute to increase level of carbon dioxide in the atmosphere and greenhouse effect.

Transesterification process is using an alcohol with the presence of catalyst to crack the molecule of oil into methyl ester or ethyl ester. Glycerol or soap will also be produced as the byproducts. Biodiesel produced via transesterification process has proven to be a viable alternative fuel with similar characteristics to diesel fuel (Ong et al. 2014). Sometime, two step involve, esterification and transesterification process, is used to low the high free fatty acid (FFA) of oil in producing biodesel. The higher the acidity content of the oil, the smaller conversion efficiency.

Biodiesel can be synthesized from a variety of feedstocks, including animal fats, vegetable oils and used cooking oils (Canoira et al. 2010). It have been a feedstock of biodiesel in great demand to recover the decreasing of fossil fuels resources. For the vegetable oil sources, it divided into two, both edible and non-edible oil. Currently, about 95% of the world's biodiesel productions are from edible oils (Gui et al. 2008) such as soybean, rapeseed, sunflower, palm, and peanut as its feedstock. However, continuous and excess use of these vgetable oils (edible oils) may cause negative impact to the world. It has an influence on global imbalance to the market demand and food supply by their high prices, reduction of food sources and growth of commercial plant capacities (Bankovic-llic et al. 2012). Thus, researchers are focusing on the non edible resources, which are not for human nutrition and could grow in arid lands. The non-edible oils are like castor, jathropha, rubber seeed, and pongamia pinnata, but for this study, castor will be used. Relevant characteristics of oils typically used for biodiesel production are given in Table 1.2.

Table 1.2 Properties of typical vegetable oils employed to produce biodiesel

Vegetable oil	Flash point (°C)	Density (kg/L)	Kinematics viscosity (mm^2/s)
Rapseed	246	0.911	37
Castor	230	0.961	227
Palm	164	0.880	36
Peanut	271	0.902	39.6
Soybean	254	0.914	32.6
Sunflower	174	0.916	33.9

Source: (Demirbas 2005)

As for the transesterification process, the catalyst is used in order to catalyse the reactions for the production of FAME from castor oil. Biodiesel production by transesterification process can be carried out using both homogeneous (acid or basic) and heterogeneous (acid, basic or enzymatic) catalysts (Sanjay et al. 2013). Traditional homogeneous catalyst (basic or acid) have advantages including high activity (complete conversion about 1h), and mild reaction conditions (around 40 °C-65 °C and atmospheric pressure) (Romero et al. 2011). By using base-catalyst, the transesterification process become faster and give very high yield in short reaction times than using the same amount of an acidic acic catalyst (Sanjay 2013).

Table 1.3 Merits and demerits of homogeneous catalyst

Type	Merits	Demerits
Alkaline catalysts	• Low cost • Favorable kinetics • High catalytic activity, very fast reaction rate, 4000 times faster than acid-catalysts • Mild reaction condition and less energy intensive	• Requirement of low FFA • Anhydrous conditions • Saponification, if the FFA contents are more than 2 wt% • Low biodiesel yield due to emulsion formation • More wastewater from purification • Non-reusable
Acidic catalysts	• Insensitive for high FFA and water contents in the oil • Catalyze esterification and transesterification simultaneously • No soap formation • Preferred for low-grade oil • Reaction occurs under mild conditions and less energy intensive	• Very slow reaction rate • Equipment corrosion • More waste from neutralization • Recycling of catalyst is problematic • Weak catalytic activity • Higher reaction temperature • Long reaction times

Source: (Azcan and Danisman 2007)

However, it generates a certain amount of water due to the reaction of hydroxide and methanol. This condition can produce hydrolysis process of the ester, and as a result, soap formation. Equation 1 shows the saponification reaction of the catalyst (sodium hydroxide) and the FFA, forming soap and water.

Equation 1

$$R^1 - COOH + NaOH \rightarrow R^1COONa + H_2O$$

R^1 = Long chain hydrocarbons (fatty acids chains)
R^1COONa = Soap

Soap can reduces the biodiesel yield and also cause significant difficulty in the separation of ester and glycrol. In order to remove the catalyst, the process is technically difficult and cause lot of waste-water to separate them and clean the products.

Therefore, heterogeneous catalyst become very important for biodiesel synthesis as it is contrast, the advantages of solid base catalyst are easy separation, simplicity in post treatments and environmentally-friendly (Guo et al. 2012). Besides, the use of it during transesterification process does not produce soaps. They are also much easier to separate from liquid products, reusable, and can be designed to give higher activity, selectivity and longer catalyst lifetimes .

Biodiesel is a common name of fatty ester. Fatty acid methyl ester has been widely used in industry. It is widely applied to leather and daily-use chemical industries and can be transformed into other esters such as esterified-ammonia, esterified-sulfonic salt and high-carbon fatty acid. In the chemical industry, leather is used to produce the leather fat-liquoring agent and sulfonic-succinate acyclic acyl ether disodium. It is serving as a promising textile detergent. High-carbon fatty alcohol can be prepared by using hydrogenised which is one of the indispensable raw materials for the production of cosmetics and perfume, for preparation of plasticizer, detergent and surface-active agent (MES) which MES is a floatation agent for mining. If saponified and acidified, it can be deoxidized into mixed fatty acid for soap and paint production. Fatty acid methyl ester can also serve as a raw material of bio-diesel which is a new environment-friendly energy source. In United States, there are using more than 200 vehicles including buses, truck, and motor boat and other than that (Kalam and Masjuki 2002).Many countries have used biodiesel to reduce the pollution, global warming environmental impact of fossil based diesel fuels (Gerpen 2007).

1.1 Motivation and Problem Statement

During the last decades, world's energy used mainly depends on fossil fuels. These sources are few in number and their production rates will begin to diminish. Moreover, high demand in energy makes their price too high due to its limitation. Besides that, continuous and huge production of energy from biodiesel synthesis from edible oils can cause negative impact to human food supply. Furthermore, there are lot of amount mussel shell waste from food industry in Malaysia.

Energy consumption mostly rely on fossil fuels. As it is non-renewable, the number reserve of fossil fuels are running out. Mussel shell waste are just thrown away from the food industrial processing without further used, make it in extremly plentiful. Biodiesel from edible vegetable oils is competing with human food chain.

1.2 Objectives

The main objectives of the research are to synthesize fatty acid methyl ester (FAME) and to examine the parameters using effect of catalyst type, catalyst loading, temperature and reaction time and catalyst recyclability on the FAME yield.

1.3 Scope of this research

Six scopes of study have been determined in this study, that is:

i. Treatment of castor oil in order to low the free fatty acid (FFA) content.

ii. Activation mussel shell waste catalyst.

iii. Combination of activated mussel shell and potassium hydroxide (KOH) through impregnated process.

iv. Characterization of solid waste basic catalyst (SWBC) using XRF, XRD, TGA and FTIR..

v. Synthesizing of FAME using SWBC based on process parameters; SWBC type (CaO, combination of CaO and KOH), catalyst loading (1, 2, 3, 4, 5 wt%), temperature (40, 50, 60, 70, 80°C) and reaction time (1, 2, 3, 4, 5hours) on FAME yield.

vi. Analysing the yield and properties of FAME based on ASTM D6751.

2 LITERATURE REVIEW

2.1 *Biodiesel*

High energy demand in the industrialized world as well as pollution problems caused due to the widespread use of fossil fuels make it increasingly necessary to develop the renewable energy sources of limitless duration and smaller environmental impact (Meher et al. 2006). One possible way to fossil fuels is the use of plant origin. This alternative can be known as biodiesel.

Biodiesel is from the combination of Greek word, bio, which means life and diesel from the famous inventor of diesel engine, Rudolf Diesel. Named by the National Soy Diesel Development Board (presently National Bio-diesel Board) which has pioneered the commercialization of biodiesel in the US during 1992 (Ramadhas et al. 2004). Biodiesel is quite similar to conventional diesel fuel, processed fuel synthesis from biological sources. Generally it is known as unharmed, renewable, non-toxic, and biodegradable in water, contains less sulphur compounds and has high flash point (Vyas et al. 2009). Biodiesel, as an alternative fuel for energy consumption, is defined as a mixture of mono-alkyl esters of long chain FAME derived from a renewable lipid feedstock such as vegetable oil or animal fat (Demirbas, 2009) (Meher et al. 2006). It is generally were investigated as diesel fuels well before the energy crises of the 1970's and early sparked renewed interest in alternative fuels (Vyas et al. 2009). It is also known that Rudolf Diesel (1858-1913), the inventor of the engine that bears his name, had used peanut oils as fuel in his invention (Gerpen and Knothe 2005). Depending upon climate and soil conditions, different nations are looking into different vegetable oils for diesel fuels. For example, soya bean oil in the United State, rapeseed and sunflower oils in Europe, palm oil in Southest Asia (mainly Malaysia and Indonesia) and coconut oil in the Philippines (Srivastava and Prasad 2000). It is very important to create new and more active plant sources whose seeds have high oil content. The most commonly used method is transesterification of vegetables and animal fat (Schwab 1988). Table 2.1 state that the properties for biodiesel.

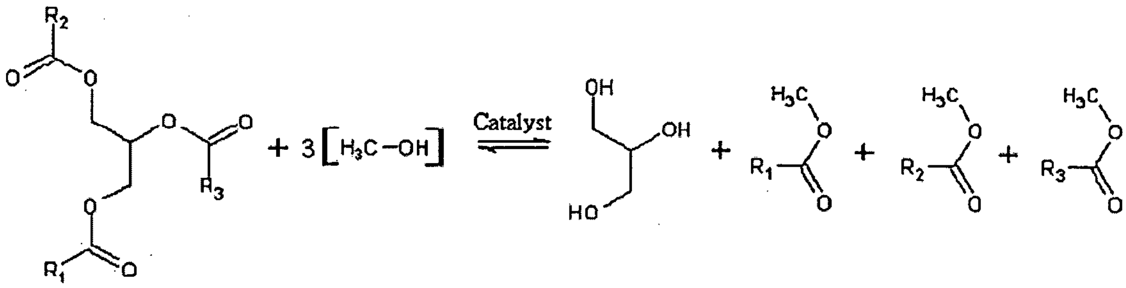
Table 2.1 Technical properties of biodiesel

Technical properties of biodiesel	
Common name	Biodiesel (bio-diesel)
Common chemical name	Fatty acid (m)ethyl ester
Chemical formula range	C_{14}–C_{24} methyl esters or $C_{15-25}H_{28-48}O_2$
Kinematic viscosity range (mm^2/s, at 313 K)	3.3–5.2
Density range (kg/m^3, at 288 K)	860–894
Boiling point range (K)	>475
Flash point range (K)	420–450
Distillation range (K)	470–600
Vapor pressure (mm Hg, at 295 K)	<5
Solubility in water	Insoluble in water
Physical appearance	Light to dark yellow, clear liquid
Odor	Light musty/soapy odor
Biodegradability	More biodegradable than petroleum diesel
Reactivity	Stable, but avoid strong oxidizing agents

Source: (Demirbas 2009)

The importance of biodiesel properties is for increasing the value in market and improving the environment. Focus on biodiesel synthesis from vegetable oils; the oils usually contain high FFA, phospholipids, sterols, water, scents and other impurities. High fuel viscosity in compression ignition is the major problem associated in use of vegetable oils as fuel (Vyas et al. 2009). Viscosity of vegetable oils is ranging 10-20 times greater than diesel fuel (Demirbas, 2008) (Balat et al. 2010). To overcome these problems, the oils need to do slight chemical modification. There are four major techniques that can be used in order to overcome the problems mention before which are transesterification, pyrolysis, emulsification and dilution. Among these, transesterification is the key and foremost important step to produce the cleaner environmentally safe fuel from vegetable oils (Meher et al. 2006) (Ong et al. 2014). Transesterification using catalyst gives high level of conversion of triglycerides to their corresponding methyl ester in short reaction time (Fukuda et al. 2001). The process of transesterification is affected by the reaction condition, molar ratio of alcohol, type of alcohol, type of amount of catalyst and the FFA and water in oils or fats (Balat 2011). The type of alcohol that can be used to produce the biodiesel is either methanol or ethanol.

The overall transesterification reaction shown as in Scheme 2.0.



Triglyceride Methanol (3) Glycerol Methyl Esters

Scheme 2.0: Transesterification reaction (Madankar et al. 2012)

Fatty acid methyl ester is the resultant of reaction between fatty acid or lipid and methanol.

There are more than 350 oil bearing crops identified whose have similar characteristics with those of diesel fuels and are compatible with material vehicle fuel system. Different oil producing crop and their yield per acre land is shown in Table 2.2.

Table 2.2 Different Edible & Non Edible Oil Producing Crops and Their Yield

Source: (Screenivas et al. 2011)

Oil Producing Crop /Plant	Yield (Lb Oil/Acre)
Palm	4585
Coconut	2072
Sunflower	734
Soybean	344
Cottonseed	250
Jatropha	1458
Castor bean	1089
Rubber seed	199

2.2 *Raw Material*

There are several types of raw materials for biodiesel production. They can come from animal fat or vegetables oil. The most common feedstock comes from vegetable oil. There are two types of vegetable oils which are edible and non-edible oils. Mostly, biodiesel production feed stocks come from edible oils since they are mainly produced in many regions and the properties of biodiesel produced from these oils are much suitable to be used as diesel fuel substitute. By converting edible oils into biodiesel, food resources are actually being converted into automotive fuels. It is believed that large-scale production of biodiesel from edible oils may bring global threat to the food supply and demand market (Gui et al., 2008). Therefore, the use of non-edible oils as a source of biodiesel nowadays is currently promoted.

2.2.1 *Castor oil*

Castor or plant *Ricinus communis L.*, as shown in Figure 2.1, popularly known as castor bean, castor oil plant, higuerilla, mamona, mamoeira, and Palma Christi is a seed of the tropical family Eurphorbiaceae (Othmer, 1979). It is originally a tree or shrub that can enlarge above 10m high, reaching an age about 4 years. It grows in humid topics to sub-topical dry zones (optimal precipitation 750-1000mm, temperature 15-38 °C) (Scholz, Silva, 2008). Castor oil is one of the top ten oils in the world and needs only 4 months for harvesting. Castor oil is viscous, pale yellow non-volatile and non-drying oil with a blend taste and sometimes us as purgative. Castor oil and its derivatives, besides being used in medicine, are used in a wide range of sectors including agriculture, textile industry, paper industry, high quality lubricants, plastics engineering, rubber and pharmaceuticals (Ogunniyi, 2006).

Figure 2-1 Castor plant

It is, one of the poisonous wild plants, with high vitality and large seed output, they survive and disperse well in barren wild fields, and are herbaceous plant with strong adaptability (Lin 2011)

Castor oil has been a feedstock in great demand by the pharmaceutical and chemical industries (Scholz et al. 2008). Castor oil is a triglyceride in which 80-90% of fatty acid chains are ricinoleic acid. Ricinoleic acid, a monounsaturated, 18-carbon fatty acid, is unusual in that it has a hydroxyl functional group on the twelfth carbon. This functional group causes ricinoleic acid (and castor oil) to be unusually polar. It is the hydroxyl group which makes castor oil and ricinoleic acid valuable as chemical feedstock. This paper deals with the FAME synthesis from castor oil with methanol that could be swap places with diesel fossil fuel for its use as a fuel in internal combustion engines. Castor (*Ricinus communis L.)* is one of the most promising non-edible oil crops, due to its high annual seed production and yield, and since it can be grown on marginal land and in semi-arid climate (Berman et al. 2011). It can be nowadays be found and cultivated in all temperature countries of the world (Nielsan et al. 2011). India is a major producer of castor seeds and has product about 163 0000 tons in 2012 (FAO 2012). Castor oil is completely soluble in alcohols and has viscosity up to 7 times higher than of other vegetable oils (Maneghetti et al. 2006) and it is a highly hygroscopic which mean water content might also high. To overcome the disadvantages, the castors oils have to be pre-treated before go through transesterification process. High FFA will result in formation of soap. Maximum amount of FFA that allowed in the system can be 2%, preferably 1%. The castor seed contain approximately about 45% to 50% of oil content and about 60% kernel, a very high potential as compared to other most commonly used oil crops in other words about 0,55 million tons of oil annually.

2.2.2 *Mussel shell*

An important contribution to the final cost production arises from the catalytic transesterification (Granados et al. 2007). Calcium oxide is an appropriate catalyst that can be used for biodiesel production. Green mussel shell is types that can synthesis the calcium carbonate to calcium oxide and can be found in Malaysia. In this study, inexpensive and environmentally-friendly catalyst was used as the catalyst is collected from the abundance waste of natural sources of calcium (Viriya-empikul et al. 2010) (Cho and Seo 2010). So far, homogenous basic catalyst mainly potassium hydroxide has been use in the production of biodiesel which is a mixture of alkyl esters. This traditional catalyst can give high activity which can complete the conversion process within 1 hour and mild reaction conditions from 40-65°C at atmospheric pressure (Romero et al. 2011). However, the use of this type catalyst leads to soap production. Therefore, development of efficient heterogeneous catalyst have been studied, which can be easily separated from reaction mixture by filtration or centrifugation and reused for several runs (Hu et al. 2011). They also are reusable, environmentally benign, noncorrosive, which show greater tolerance to water and free fatty acid (FFA) in feedstock, improve biodiesel yield and purity, have simpler purification process for glycerol and are easy to separate from the biodiesel product (Gimbun et al. 2013). The mussel shell is an aquatic bivalve mollusk, similar to their marine clam and oyster and it has two shells connected by hinge-like ligament (Hu et al. 2011).

Figure 2-2 Mussel shell waste

2.2.3 Potassium Hydroxide (KOH)

Potassium hydroxide used for this research is an inorganic compound with the formula of KOH. It is colourless solid and called as a prototypical strong base. Furthermore, this solvent usually sold as translucent pellets which will become tacky in air because the element inside KOH is hygroscopic. Consequently, KOH typically contains varying amounts of water and dissolution in water is strongly exothermic meaning that the process gives off significant heat. Potassium hydroxide concentrations approximately about 0.5 to 2.0% are irritating when coming in contact with the skin while concentrations higher than 2% are corrosive.

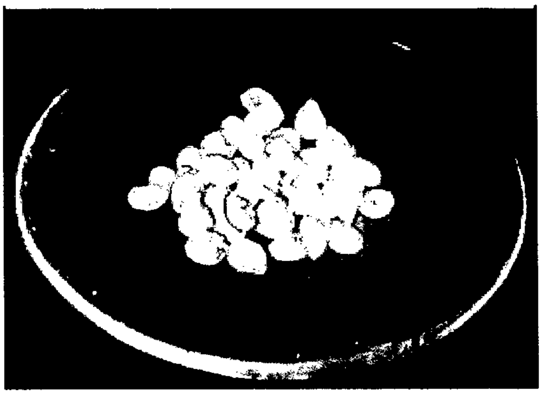


Figure 2-3 Pellets of potassium hydroxide (KOH)

2.2.4 Methanol

Methyl alcohol used in this experiment also known as wood alcohol, wood naphtha, wood spirits, or methanol is a chemical compound with the molecular formula CH_3OH. It is a flammable chemical compound, colourless with a strong odour. Methyl alcohol dissolves in a wide range of non-polar compounds. The boiling point for this solvent could be achieved at 64.7°C. Thus, it is used widely as a solvent transesterification and as a cleaning fluid, especially for dissolving oils.

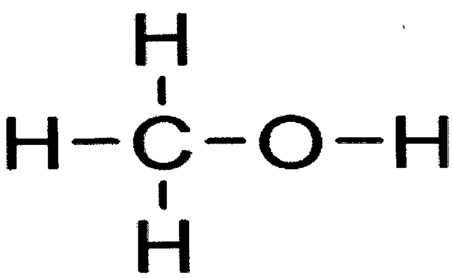


Figure 2-4 Structural formula of methyl alcohol

2.3 Catalyst

A substance that speeds up a chemical reaction, but it is not consumed by the reaction; hence the catalyst can be recovered unchanged at the end of the reaction. A catalyst is usually used in order to improve the reaction rate and yield (Ma and Hanna 1999). Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst. Catalyst used in the transesterification of triglycerides can be classified as homogeneous, heterogeneous and enzyme catalyst.

Heterogeneous catalysis has a different phase than the reactants. They are more economical and ecologically friendly. Heterogeneous catalysts are also easier to separate from liquid products and can be designed to give higher activity, selectivity and longer lifetimes (Tanabe and Holderich 1999). Because of these advantages, the number of researchers using solid bases as a catalyst has increased over the past decade. The use of heterogeneous catalysts does not produce soap through free fatty acid neutralization and triglyceride saponification. The most commonly studies for heterogeneous basic catalysts are alkaline metals carbonates (Na2CO3, K2CO3), supported alkali metal ions, alkaline earth oxide (CaCO3), and metal oxides (CaO, MgO, SrO, BaO) (Verziu *et al.* 2009).