# EGGSHELL CATALYST ASSISTED PALM BIODIESEL PRODUCTION FOR BLENDING OF B10 BLENDED DIESEL FUEL

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**WHOLEHEARTEDLY DEDICATED TO MY BELOVED PARENTS,**

**ALL THAT I FOUGHT AND OVERCAME,**

**YOU ARE IN MIND.**

**ALWAYS.**

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## ABSTRACT

Palm biodiesel is currently being internationally debated, more so in Malaysia. The study of this field is increasing day by day in finding ways to reduce its production cost. This study was conducted to analyze the trend of different calcination temperatures to the production of calcium oxide catalyst derived from waste eggshells. The temperatures used are 900°C, 920°C and 950°C. Three different samples of CaO powders were then tested with SEM for surface morphology, XRD for phase present in powders and FTIR to determine presence of bands. The best catalyst is selected to assist the palm biodiesel production through transesterification method. The transesterification method consists of varying parameters of molar ratios (9:1, 12:1 and 15:1) and catalyst content (2%, 3% and 4%), with fixed parameters of 65°C reaction temperature and 600rpm stirring speed. Nine samples were made, and each sample were tested for their physical properties in accordance to the ASTM D6751 standard. The best sample was produced in bulk and blended into EB10 (10% bio-content diesel). The biodiesel blend was also tested for its properties which includes water content, kinematic viscosity, flash point, density and ester content. Lastly, the blended diesel EB10 is compared to a local station B10 diesel blend for its physical properties. It is found that calcination temperature of 920°C is determined to be the most optimum as it gives out the higher yield of calcium oxide while using less energy consumption. For transesterification, parameters with 12:1 molar ratio, 4 wt.% catalyst content are deemed to be the most optimum which yielded 98.89% of biodiesel. This blended diesel blend EB10 was also tested for its properties and found out that it is safe to be applied daily. The blend was also compared to the quality of market available petroleum diesel from a local petrol station and found to have the same quality to it. As for recommendations, further research by using higher blends of biodiesel (B15 or higher) should be study with the same eggshell catalyst synthesized.

**ABSTRAK**

Biodiesel kelapa sawit kini menjadi topik debat hangat di medan antarabangsa lebih-lebih lagi di malaysia diesel semasa, lebih-lebih lagi di Malaysia. Penyelidikan dalam bidang ini semakin hari semakin rancak untuk mencari cara mengurangkan kos pengeluarannya. Kajian ini dijalankan untuk menganalisis arah aliran perubahan suhu rawatan haba pengkalsinan pemangkin kalsium oksida, yang diperolehi daripada sisa kulit telur. Suhu pengkalsinan yang digunakan ialah 900°C, 920°C dan 950°C. Tiga sampel CaO yang dihasilkan dari kulit telur telah diuji dengan SEM untuk melihat struktur morfologi permukaan, ujian XRD untuk menentukan fasa yang wujud dalam sampel dan FTIR untuk menentukan kewujudan jalur dalam sampel. Pemangkin yang terbaik kemudiannya digunakan untuk menghasilkan biodiesel melalui proses transesterifikasi. Transesterifikasi melibatkan tiga nisbah molar (9:1, 12:1 and 15:1) dan tiga kandungan pemangkin (2%, 3% and 4%), 65°C suhu reaksi tetap dan 600rpm kelajuan tetap. Sembilan sample terhasil dan sifat fizikal setiap sample diuji mengikut piawaian ASTM D6751. Sample yang terbaik dipilih dan dihasilkan secara pukal untuk menghasilkan EB10 (diesel dengan 10% kandungan bio). Sampel ini juga telah diuji sifatnya yang merangkumi ujian kandungan air, tahap kelikatan, titik kilat, ketumpatan dan kandungan ester. Seterusnya, campuran diesel EB10 dibandingkan dengan campuran biodiesel yang diperolehi dari stesen minyak tempatan. Didapati bahawa suhu kalsinasi 920°C ditetapkan sebagai yang suhu paling optimum kerana memberikan hasil kalsium oksida yang lebih tinggi dengan penggunaan tenaga yang rendah. Parameter dengan nisbah molar 12:1, 4% kandungan pemangkin dipilih sebagai parameter paling optimum kerana telah menghasilkan biodiesel dengan 98.89% kandungan bio. EB10 yang terhasil diuji sifatnya, didapati ia telah menepati piawaian dan selamat diguna. Bagi cadangan penyelidikan seterusnya, campuran biodiesel yang lebih tinggi (B15 dan keatas) boleh dihasilkan dengan menggunakan pemangkin kulit telur yang telah dihasilkan.

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# LIST OF ABBREVIATIONS AND SYMBOLS

| | | |
|---|---|---|
| UTHM | - | Universiti Tun Hussein Onn Malaysia |
| US | - | United States |
| KTMB | - | Kereta Api Tanah Melayu Berhad |
| FFA | - | Free Fatty Acid |
| ASTM | - | American Society for Testing and Materials |
| IUPAC | - | International Union of Pure and Applied Chemistry |
| EN | - | European Standards |
| ENISO | - | Europe International Organization for Standardization |
| FAME | - | Fatty Acid Methyl Esters |
| SEM | - | Scanning Electron Microscope |
| XRD | - | X-ray Diffractometer |
| FTIR | - | Fourier Transform Infrared Spectroscope |
| GC-FID | - | Gas Chromatography Flame Ionization Detector |
| B0 | - | Pure Diesel (Zero Bio-content) |
| B6 | - | Biodiesel with 6% Bio-content |
| B10 | - | Biodiesel with 10% Bio-content |
| EB10 | - | Eggshell Biodiesel Blend |
| B20 | - | Biodiesel with 20% Bio-content |
| B100 | - | 100% Bio-content |
| OH | - | Hydroxide |
| $CaCO_3$ | - | Calcium Carbonate |
| NaOH | - | Sodium Hydroxide |
| KOH | - | Potassium Hydroxide |
| $CH_3NaO$ | - | Sodium Methoxide |
| $NaNH_2$ | - | Sodium Amide |
| $KNH_2$ | - | Potassium Amide |

| | | |
|---|---|---|
| KH | - | Potassium Hydride |
| Mg | - | Magnesium |
| Ca | - | Calcium |
| Sr | - | Strontium |
| Ba | - | Barium |
| CaO | - | Calcium Oxide |
| °C | - | Degree Celsius |
| °C/min | - | Degree Celsius per Minute |
| Rpm | - | Rotation per Minute |
| g | - | gram |
| g/mol | - | Gram per mol |
| g/mL | - | Gram per milliliter |
| mL | - | Milliliter |
| wt.% | - | Weight Percent |
| ρ | - | Density |
| $cm^3$ | - | Centimeter Cube |
| kPa | - | Kilopascal |
| kg | - | Kilogram |
| RM | - | Ringgit Malaysia |
| MJ | - | Megajoules |
| GJ | - | Gigajoules |
| ppm | - | Parts per million |
| $mm^2/s$ | - | Millimeter cube per second |
| $kg/m^3$ | - | Kilogram per meter cube |

# LIST OF APPENDICES

# CHAPTER 1

# INTRODUCTION

## 1.1 Background of study

There are two terms that always brings misconception to consumers, the terms are biofuel and biodiesel. The society thought that fuel and biodiesel are the same thing but are two very different materials. Biofuel is derived from two English words, biology and fuel. The biological terms show that the sources are naturally obtained and has the potential to become an energy source, such as plants, animals and certain mass of gas (US Energy Information Administration). Biofuel is pure vegetable oil without any mixture of diesel. It is 100% clean vegetable oil extracted from biological sources and its biomass energy can be kept for a long period of time without causing harm compared to conventional fuel such as petroleum and coal (Malmgren et al., 2012).

As for biodiesel, it is a type of bioenergy or biofuel which is commonly used in the Europe and internationally due to its availability and renewability. Biodiesel is a renewable, clean-burning diesel replacement that can be used in existing diesel engine without modifications (National Biodiesel Board, 2013). It is produced from oil and fats through a process known as transesterification that produces methyl or ethyl esters with glycerol. Biodiesel could be produced from methyl and ethyl esters raw materials (Zahan, 2018). Examples of raw materials for biodiesel production are rapeseed oil, palm oil, sunflower oil, soybean oil, corn oil and olive oil. The advantages of biodiesel compared to petroleum is that it is nature friendly, contains low sulphur dioxide and carbon dioxide content, non-toxic, safe and does not need any engine modification to be used where it is compatible to most diesel engines. In addition, it is also one of the sources which could be renewed and marketed domestically and internationally (Innocent et al., 2013).

Conventionally, triglyceride transesterification uses homogeneous catalyst such as NaOH, $CH_3NaO$, KOH, $NaNH_2$, $KNH_2$ and KH. But now, heterogeneous catalysts are being used due to its abundant advantages over homogeneous catalysts and previous research shows that heterogeneous catalyst shows good results in biodiesel production (Thangaraj et al., 2018).

Advantages in using heterogeneous catalyst is that it does not corrodes and could be easily separated from the fluids. In fact, heterogeneous catalyst could be used in biodiesel production for oils that has high content of free fatty acids (FFA). Oil feedstock that was commonly use in Malaysia are palm oil as this is the main production of the country, easily obtained and cheap. As for other countries such as the United States, common feedstock use for biodiesel productions are canola oil, soybean oil and tallow (US Department of Energy, 2019).

Currently, transesterification is the preferred choice in producing biodiesel. It is a process that mixes oils (vegetable oil/ animal fats) with alcohol (mostly using methanol or ethanol) with the presence of catalyst to change it into ester fats. This mixture is separated into two parts, the glycerine and alcohol mixture, and esters. Glycerine with higher density will sink while the alcohol ester mixture with lower density will float (Soudagar et al., 2018). Moreover, the alcohol and ester mixture need to undergo a separation process. Alcohol obtained could be stored and reused. Meanwhile the ester obtained is sent to be cleaned and filtered. The clean ester is the biofuel. This biofuel could be used directly or mixed with diesel before used as fuel.

Another element which is taken into account in producing biodiesel is to make sure that the biodiesel produced is on par with the fixed international standard. This standard is currently being use everywhere in the world. The standard is from the American Society for Testing and Materials (ASTM) D6751 as shown in Appendix A and Appendix C.

## 1.2 Problem statement

Previous study shows that calcium-containing catalyst has shown advantages such as good catalytic activity and reusability (Kawashima et al., 2018). However, further study on calcination temperature is yet to be done for the catalyst to be used in transesterification of palm oil. Therefore, this study contains 3 important scopes which includes the selection of the optimum calcination temperatures for eggshell catalyst, synthesizing of biodiesel catalysed by the eggshell catalysts produced, obtaining the FAME yield as well as attempting to safely blend B10 diesel fuel.

There are a number of natural calcium resources that could be made into powdered catalyst, such as clams, cockle shells, fish bones as well as eggshells. This study further investigates the production of this catalyst by using waste eggshells collected from local hawker stalls. Three different calcination temperature is used in this research. The best catalyst outcome is then used to assist the transesterification of palm oil.

Palm oil is chosen as oil base as it has very low Free Fatty Acid (FFA) content. The free fatty acid (FFA) value for palm oil is 1.128%, hence the extra step of esterification in the biodiesel production could be neglected (Azeman et al., 2015). Eggshell catalyst is seen to be one of the solutions to reduce the production cost of palm biodiesel production due to it is easily obtained and cheap. To further study on the ways to reduce the production cost of biodiesel production, the transesterification process is done with different parameters of molar ratios and catalyst content to obtain the optimum recipe to produce palm biodiesel.

The overall process is futile if the biodiesel produced does not comply with the international standard set, therefore biodiesel properties test is done. The commonly used international standard are the American Society for Testing and Materials (ASTM) D6751 and European Standard (EN) 14214. The properties tested are density, kinematic viscosity, percentage of water content, ester content and flash point.

B10 diesel fuel is currently the biodiesel fuel blend currently being produce in Malaysia, therefore this study aims to blend B10 diesel fuel by using the biodiesel produced from the transesterification reaction with eggshell catalyst. The new blend of B10 named EB10 (abbreviation for Eggshell B10) is compared to the existing B10 diesel fuel sold in the market in terms of its physical characteristics. Analysis is done to see whether the blended biodiesel has as good quality as the one sold commercially and whether it is safe to be used in vehicles. Along these lines, this mixture of biodiesel can help in controlling air pollution and facilitate the weight on rare resource without fundamentally sacrificing engine power and economy.

## 1.3 Significance of study

The use of heterogeneous catalysts for biodiesel production has become a focus as it offers many advantages such as reducing the purification costs and related environmental impacts such as water pollution and resources shortage crisis (Hajjari et al., 2017). Calcium-containing catalyst was identified as an interesting heterogeneous catalyst for biodiesel production (Lani et al., 2019). The purposes of this study is to prepare and characterize the catalysts for biodiesel production, to determine the biodiesel yields from palm oil transesterification reaction using calcium-containing catalysts and lastly blending the biofuel to pure diesel with fixed ratio to blend an in-house made B10 biodiesel fuel which is safe to be applied on vehicles.

A catalyst may increase or decrease the reaction rate, may influence the direction or selectivity of a reaction, and the amount of catalyst consumed by the reaction is negligible compared to the consumption of reactants. Knowing these values, could indirectly reduce the cost of biodiesel production in the present market.

## 1.4 Objectives of study

(i) To prepare the catalysts from waste eggshells by using the selected optimum calcination temperature.

(ii) To produce palm biodiesel by using the optimum parameters selected for blending of B10 diesel fuel.

## 1.5 Scope of study

(i) The scope from the first objective is catalyst preparation. Powders of calcium oxide is to be synthesized by converting them from waste recycled eggshells collected from a local hawker stall. Eggshells were cleaned, dried, ground, and calcined. Three different calcination temperature (900°C, 920°C and 950°C) are used and hence resulted in three CaO powder samples. Samples were analyzed, characterized, and optimize.

(ii) The second scope is transesterification of palm oil with the optimum eggshell catalyst made. A total of 9 different parameters with varying methanol to oil ratios (9:1, 12:1 and 15:1) and catalyst content (2%, 3% and 4%) were conducted. The fixed parameters are 65°C reaction temperature and 600 rpm stirring speed.  samples were made to identify the most optimum reaction parameters to produce biofuel.

(iii) The samples of transesterification reaction are tested for its properties which includes water content, kinematic viscosity, density, flash point and fatty acid methyl ester content. These properties were tested to check if they comply with the international standard for biodiesel. The standard used are ASTM D6751 and EN14214. Next, the most optimum biofuel is then produced in bulk and blended with pure diesel (B0) to produce our own EB10 (Eggshell B10) biodiesel with 10% bio-content. The blended diesel fuel is then compared with a local bought B10 diesel fuel to compare it for its physical properties.

(iv) The EB10 blended diesel fuel is tested for its properties to verify that the blend is safe to be used and in standard with the ASTM D6751 and EN14214 international standard.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

Common fuel that the world is using currently is made of natural resources such as petroleum and coals categorized as fossil fuels. These fossil fuels are reducing as days go by and are close to depletion, thus an alternative should be found in exchange. Due to the lack of supply and intricate manufacturing processes besides needing a ginormous plant, therefore fossil fuels cost higher and become a burden to consumers (Martin et al., 2017).

Nowadays, biodiesel is coming into the spotlight due to its properties which is much safer and has the same combustive ability as fossil fuels. It is also an alternative resource because of its smaller production cost and the natural resources are vastly available (US Department of Energy, 2019). Biodiesel could be produced from vegetable oils such as palm oil, soybean oil, rapeseed oil and coconut oil, it could also be made from animal's fat and used cooking oil (Hassan et al., 2013).

Green catalyst meant for biodiesel production is also becoming the centre of attention due to its reusability, cheap price and most importantly the good environmental effect such as recyclability and reduction of waste.

## 2.2 Biodiesel

Materials utilized to produce biodiesel are vastly derived from vegetables, fats and waste oils. Biodiesel is an alternative to replace the present diesel minerals. Currently, biodiesel is a clear choice because it has low carbon dioxide release and is very nature friendly (Pennstate, 2019). Biodiesel made from vegetable oil has more advantage compared to the other raw materials. The advantages include heat rate of 80% of the mineral diesel, easily obtained and could be renewed (Chidambaranathan et al., 2019). Besides that, biodiesel is also a kind of lubricant, less toxic but has high combustion rate, zero sulphur content, high cetane value and low exhaust emissions. It was found that replacing mineral diesel by pure biodiesel fuel has lowered the service-life mileage of the engine-lubricant oil charge from 20,000 to 13,000 km for mono-articulated buses, and from 15,000 to 10,000 km for bi-articulated ones. Therefore, this mileage was reduced to approximately two-thirds of the value recommended for vehicles fueled by conventional diesel (Pereira et al., 2020). Biodiesel produced has high value of viscosity and at the same time has low volatility and create non-fixed hydrocarbon chain (Luque et al., 2011).

As a way to reduce the price of biodiesel, raw materials from oil wastes is introduced due to its lower price in compared to the other raw materials. Waste oil is one of the best alternatives to produce biodiesel after vegetable oils (Chidambaranathan et al., 2019).

After all this while, most catalysts used to produce biodiesel are homogeneous. However, this type of catalyst possesses a significant disadvantage, such as difficulty to be separated from the product as this type of catalyst dissolves in the biodiesel and fully dissolves in glycerol. This will indirectly result in rusting of metal of the machine as well as contaminating the surrounding environment. In addition, to separate the catalyst from the product, it will take more steps and indirectly increases the cost of manufacturing it (Nath et al., 2019).

Few efforts are made to reduce the negative effects of the homogeneous catalyst in biodiesel production. One of the most commonly applied is, exchanging it with another type of catalyst which is heterogeneous catalyst. Hence, more research in using heterogeneous catalyst should be made in the field of biodiesel production so that it will produce a more productive and consumer friendly biodiesel. Heterogeneous catalyst is significantly easier to be separated and it could be reused repeatedly which will then cut the cost of the whole process of biodiesel production (Boey et al., 2011).

Previous research uses raw material waste to produce calcium-based catalyst as it will further reduce the production cost. Calcium resources could be obtained from nature, which is not being used anymore such as eggshells, cockle shells as well as bones. Cockle shells are selected as a calcium source which shows great potential as a cheap catalyst for biodiesel production. From the observation, cockle shells are used as an alternative source for CaO catalyst. Cockle shells could be combusted in high heat from 700°C until 1000°C. After that, it could be safely used in the transesterification of cooking oil with methanol solvent (Buasri et al., 2013). But as for this research, further study is conducted on the usage of waste recycled eggshells as a raw material in different calcination temperature for calcium oxide powder catalyst.

## 2.3 Catalyst

Catalyst is used as a complementary in the production of biodiesel. There are two general types of catalysts, the conventional homogeneous catalyst, and the heterogeneous catalyst (Guldhe et al., 2017). Catalyst is a substance or additive material to a reaction which aids in bringing up the rate of chemical changes without being used up or depleted and could be recovered at the end of the chemical reaction (IUPAC Gold Book, 2019).

The presence of catalyst does not alter the equilibrium of a chemical reaction, but it only helps in increasing or decreasing the speed (IUPAC Compendium of Chemical Terminology, 2009). The usage percentage of catalyst to be used is dependent on the Free Fatty Acid (FFA) content and quality of raw material which falls in between 0.5 and 1.5% (Luque et al, 2011).

For raw materials with low quality and high FFA values, a good acidic catalyst is needed during esterification process. There are quite a number of raw materials being used by previous study as a source for calcium oxide production, Table 2.1 below shows different raw materials with their respective optimum calcination temperature. In this study, different calcination temperature of eggshell calcium oxide powders is used as catalyst. This is based on the study conducted, where 98.56% of eggshells are converted into calcium oxide, showing that eggshells are a good source for calcium oxide production (Ahmad et al., 2015).

Table 2.1: Different Raw Materials with Optimum Calcination

| Raw Materials | Optimum Calcination Temperature | Author/Reference |
|---|---|---|
| Mussel Shells<br>Cockle Shells<br>Scallop Shells | 1000°C | Buasri et al., 2013 |
| Fish Bones | 900°C | Widiarti et al., 2017 |
| River Snail Shells | 800°C | Kaewdaeng et al., 2017 |
| Fly Ash / Sheep Bone | 900°C | Volli et al., 2019 |
| Angel Wings Shell | 900°C | Syazwani et al., 2019 |
| Goat Bones / Cockle Shell | 900°C | Lani et al., 2019 |
| Golden Apple Snail Shell | 800°C | Trisupakitti et al., 2018 |

### 2.3.1 Homogeneous catalyst

Homogeneous catalysts are catalysts present in the same phase as the substances that go into the chemical reaction phase. These types of catalysts also retain its chemical state during reaction but however may or may not undergo changes in physical states such as in sizes or colours (Arzamendi et al., 2007). The homogeneous forms of a catalyst are nothing but chemical compound that stays in the same phase as the reactants and help in the acceleration of chemical changes. These chemicals help to achieve equilibrium quicker by increasing the rates of both the forward and reverse reactions. Furthermore, in many homogeneous catalytic processes the ligands present in the catalyst needs to be discarded or separated by a few methods so that these catalysts would not be wasted and converted to another homogeneous catalyst for future uses and applications (Wang et al., 2014).

In the industry, the separation of these types of soluble catalyst from the reacting phase or mixture is carried out by distillation, which could be either by flash distillation or distillation which is external to the reacting medium. During flash distillation, the reaction is carried out in higher temperature, to help evaporate the product in a continuous manner and at the end collects the remaining catalyst. Due to high temperature process, it leads to catalyst decomposition. Hence, the maximum temperature is always controlled throughout the process in order to contain the decomposition. In short, the process of separating the homogeneous catalyst from the substance or mixture takes longer time and greater cost (Arzamendi et al., 2007).

### 2.3.2 Heterogeneous catalyst

In chemical terms, a heterogeneous catalyst refers to a form of catalyst where the phase of the catalyst differs from the reactants in chemical reaction. The phases here refer not only to solid, liquid and gas but also immiscible liquids such as oil and water. The great majority of heterogeneous catalysts currently in practical uses are solids and the great majority of reactants are liquids or gases (Chmielarz et al., 2018). However, majority of heterogeneous catalyst are solids and many variations exist, such as solid and gas phases, solid and solution phases as well as immiscible liquid phases (Bailie et al., 2001).

A catalyst that is in a separate phase from the reactants is said to be a heterogeneous or contact catalyst. Contact catalysts are materials with the capability of absorbing molecules of gases or liquids to their surfaces. For example, heterogeneous catalyst is the use of finely divided platinum to catalyse the reaction of carbon monoxide with oxygen to form carbon dioxide. This reaction is generally applied in automobiles located in the catalytic converters mounted in cars to eliminate carbon monoxide from exhaust gases.

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