

TRANSESTERIFICATION OF PALM OIL WITH METHANOL
USING BARIUM OXIDE

MUHAMAD ZAHRUL BIN GHAZALI

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ABSTRACT

Transesterification is a transformation of ester into biodiesel accelerated with catalysts. Biodiesel or biofuel is a great solution in greenhouse problems emitted by petroleum diesel. Unlike underground oil reserves, biofuels are a renewable resource since crop can always grow and turn into fuel. Using Barium Oxide as solid catalyst is to counterpart problems by homogenous catalyst which require more energy in washing process for separation which lead to more waste. The present studies aimed to determine the conversion of methyl ester produced and the optimum operation condition for the transesterification process. The research study is done in a batch reactor system. Optimum operating condition is at 50°C with molar ration of palm oil to methanol is 1:15 and with catalyst loading of 3 wt%. The highest conversion of methyl esters from this optimum operating condition is 84.15%.

ABSTRAK

Proses pengesteran ialah perubahan ester kepada biodiesel yang menggunakan pemangkin untuk meningkatkan kadar tindak balas. Biodiesel atau bahan bakar biologi adalah satu jalan penyelesaian kepada masalah rumah hijau yang disebabkan oleh minyak petroleum. Tidak seperti simpanan minyak bawah tanah, biodiesel adalah sumber yang boleh dikitar semula kerana penanaman semula boleh dilakukan dan ditukar menjadi biodiesel. Menggunakan Barium Oksida sebagai pemangkin pepejal adalah untuk mengelak masalah yang ditimbulkan oleh pemangkin yang larut dalam fasa yang sama di mana memerlukan lebih banyak tenaga semasa proses pembasuhan untuk proses pemisahan. Kajian terkini tertuju kepada mencari peratusan penghasilan Metil Ester dan keadaan optima atau ternaik untuk penghasilan melalui proses pengesteran ini. Kajian ini dijalankan menggunakan sistem reaktor batch. Dari skop kajian, dapat dibuktikan bahawa keadaan optima dapat dicapai pada suhu 50°C dengan nisbah 1:15 molar minyak masak kepada metanol dan 3 wt% penggunaan pemangkin. Peratusan penghasilan tertinggi metal ester melalui kaedah optima ini ialah sebanyak 84.15%.

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LIST OF ABBREVIATIONS

Al	Aluminium
BaO	Barium Oxide
C _{FA0}	Initial Concentration
C _{FA}	Final Concentration
CaO	Calcium Oxide
CH ₃ OH	Methanol
CO ₂	Carbon Dioxide
CTAB	Cetyltrimethyl Ammonium Bromide
DG	Diglycerols
FFA	Free Fatty Acid
FID	Flame Ionization Detector
GC	Gas Chromatography
H	Hydrogen
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
K/ZrO ₂	Tungstated Zirconium Dioxide
KOH	Potassium Hydroxide
La ₂ O ₃	Lathanium Oxide
MCM-41	Mobile Composition Matter-41
Mg	Magnesium
MG	Monoglycerols
MgO	Magnesium Oxide
N ₂	Nitrogen
NaOH	Sodium Hydroxide
O	Oxygen
PPL	<i>Pig pancreatic</i> Lipase
RML	<i>Rhizomucor miehei</i> Lipase
SrO	Strontium Oxide
T	Temperature
TEOS	Tetraethylorhosilicates
TG	Triglyceride/Triacylglycerols
TiO ₂	Titanium Dioxide
W	Weight

X_{FA}	Conversion
ZnO	Zinc Oxide
ZrO ₂	Zirconium Dioxide

LIST OF SYMBOLS

°C	Degree Celcius
µg	Micro Gram
µL	Micro Liter
m	Meter
kg	Kilogram
wt	Weight
mg	Miligram
h	Hour
min	Minute
g	Gram
µm	Micrometer
rpm	Revolutions per Minute
mL	Mililiter
ppm	Part per Million
m ³	Meter cube

CHAPTER ONE

INTRODUCTION

Stringent environmental rules and legislation governing worldwide and recent awakening to the realization of dismal scenario of fossil fuel availability have led to the emergence of renewable fuels. The Malaysia National Biofuel Policy was launched on 21 March 2006 having envisions in use of environmentally friendly, sustainable and viable sources of energy to reduce the dependency fossil fuel and enhanced prosperity and well-being of all the stakeholders in the agriculture and commodity based industries through stable and remunerative prices. A wide range of alternatives have been developed – from hydrogen based vehicles to natural gas vehicle. However, one of them has been effective as biofuels – ethanol and biodiesel – both from commercial as well as environmental perspective.

Feedstocks for biodiesel production vary considerably with location according to climate and availability. Generally, the most abundant lipid in a particular region is the most common feedstock. This, rapeseed oil is predominantly used in Europe, palm oil predominates in tropical countries such as in Malaysia and soybean oil and animals fats are primarily used in the United States. However, many of these oils are prohibitively expensive and have competing food-related uses. Consequently, the development of alternative feedstocks for biodiesel production that meet all or most of the following criteria has attracted considerable research attention: high oil content, low agricultural inputs, favorable fatty acid composition, compatibility with existing farm equipment and infrastructure, production in sustainable fashion in off-season or in agriculturally undesirable lands, definable growth seasons, and uniform seed maturation rates.

There are several feedstocks as raw material that can be used for the process of biodiesel. Sugar cane as example, which is a major cultivation in Brazil. Brazil is the leader in sugarcane ethanol fuel and the largest exporter of ethanol. Ethanol is to be the substitute for gasoline for the main car fuel that can use around the globe. Then, there is also corn or maize for the feedstock of biodiesel which is cultivated mostly in United States and Brazil. In US, they had done an ethanol program and justified to eliminate additives on gasoline and cutting down on global warming gases. Other than that, rapeseed or canola is also used as one of the feedstock for biodiesel process. The major cultivation regions are EU, China, Canada and India. In Europe, rapeseed counts for 80% of biofuel production. Even though this plantation is not a food crop, the cultivation needs fertilizers and good soils. Palm oil also used in biodiesel production which Indonesia and Malaysia is regions with a major cultivation. Palm oil based biofuels provides a high quality fuel blend with fossil fuels such as petroleum.

Global demand for edible oil is increasing in the few decades which cause a tremendous increase in the area of oil crop cultivation especially soybean and oil palm. The world production of palm oil is 45 million tones and highest production is in South East Asia with a total 89% of total palm oil production (40% in Malaysia, 46% in Indonesia, 3% in Thailand) (Shuit *et al.*, 2009).

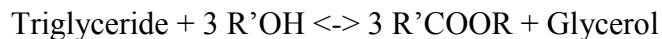
1.1 BACKGROUND OF THE STUDY

Biofuels have been around as long as cars have. At the start of the 20th century, Henry Ford planned to fuel his Model Ts with ethanol, and early diesel engines were shown to run on peanut oil. But discoveries of huge petroleum deposits kept gasoline and diesel cheap for decades, and biofuels were largely forgotten. However, with the recent rise in oil prices, along with growing concern about global warming caused by carbon dioxide emissions, biofuels have been regaining popularity. There are various ways of making biofuels, but they generally use chemical reactions, fermentation, esterification, transesterification, and heat to break down the starches, sugar, and other molecules in plants. The leftover products are then refined to produce a fuel that cars can use. Countries around the world are using various kinds of biofuels. For decades, Brazil has turned sugarcane into ethanol, and some cars there can run on pure ethanol rather than as additive to fossil fuels.

From such facts, biofuels look like a great solution. Cars are a major source of atmospheric carbon dioxide, the main greenhouse gas that causes global warming. But since plants absorb carbon dioxide as comes out of the tailpipes of cars that burn these fuels. And unlike underground oil reserves, biofuels are a renewable resource since we can always grow more crops to turn into fuel.

The term biodiesel refers to the alkyl esters of fatty acids produced from vegetable oil, animal fats and recycled greases when used as fuel for diesel engines. Biodiesel is most commonly produced by the transesterification of acylglycerols with an alcohol, usually methanol, in the presence of an alkaline catalyst. More recently, noncatalytic processes utilizing supercritical alcohols have been employed.

When vegetable oils are used as the feedstock, three consecutive reactions give rise to the formation of the fatty acid esters. The overall transesterification reaction proceeds as equation below



On the basis of the above reaction, it is clear that one mole of triglyceride will yield three moles of fatty acid esters and one mole of glycerol as a byproduct. The pure fatty acids can then be used as a feedstock for biodiesel production.

Biodiesel is commonly derived from triglycerides and methanol through transesterification using homogenous catalysts, such as alkali hydroxides (NaOH and KOH), carbonates, and sodium and potassium alkoxides. The properties of biodiesel are similar to those of petro-diesel fuels. The viscosity is the most valuable property of biodiesel fuels since it has tremendous effects on the operation of fuel injection equipment, particularly at lower temperature where an increase in viscosity affects the fluidity of the fuel. It was also discovered that higher viscosity leads to poorer atomization of the fuel spray and which affects accuracy of the operation of fuel injectors.

Biodegradability of biodiesel has been considered to be a solution for waste accumulation leading to environmental pollution. Demirbas (2008) stated that biodegradable fuels such as biodiesels have a wide range of potential applications and they are environmentally friendly. The author revealed that there is growing interest in degradable diesel fuels that degrade faster than the traditional disposable fuels. It was stated that biodiesel is non-toxic and degrades about four times faster than petro-diesel. Also its oxygen content improves the biodegradation process.

The use of millions of vehicle across the globe especially in big cities and towns contribute a lot in generating gaseous emissions, hence polluting the environment. These emissions referred to as green house gases are attributed to the cause of global warming. Green house gases such as carbon-dioxide, carbon monoxide, nitrogen oxide, and sulfur causes climatic distraction resulting in drought and environmental adversities and both fauna and flora.

The application of biodiesel to our diesel engines for daily activities is advantageous for its environmental friendliness over petro-diesel. The main advantageous of using biodiesel is that it is biodegradable, can be used without modifying existing engines, and produces less harmful gas emissions such as sulfur oxide. It can be concluded that the advantages of biofuels over fossil fuels to be: (a) availability of renewable sources; (b) representing CO₂ cycle in combustion; (c) environmentally friendly; and (d) biodegradable and sustainable. Other advantages of biodiesel are as follows: portability, ready availability, lower sulfur and aromatic content, and high combustion characteristics.

1.2 PROBLEM STATEMENT

Despite the environmental advantage of the biodiesel, production cost of biodiesel is pretty high compared to conventional diesel fuel. In order to reduce the production cost, used vegetable oils has been suggested as feedstock. However the free fatty acids in used vegetable oils are known to cause severe problems for the transesterification catalyzed by base catalyst. Free fatty acids can react with the base catalyst (neutralization reaction), which brings a loss of catalyst and a production of soap as by-product which accelerates the deactivation of the base catalyst (Park *et al.*, 2008).

The most widely used industrial method for the commercial production of biodiesel from vegetable oils/fats is a base catalyzed transesterification process using KOH or NaOH as the homogeneous catalyst and MeOH as the lower alcohol. The advantage of this process is production of methyl esters at very high yields. Several oils, both edible and non-edible such as sunflower oil, palm and jatropha have been transesterified for biodiesel production. However, major quality related problems were encountered and it was main hindrance for large scale industrial production of biodiesel by homogeneously catalyzed transesterification.

Biodiesel synthesis using solid catalysts instead of homogeneous liquid catalysts could potentially lead to economical production cost because of reuse of the catalysts (Suppes *et al.*, 2004). Additional benefit with solid catalyst is the lesser consumption of catalyst. Other than that, heterogeneous catalysts are solid and it can be separated from the product by filtration, which reduces the washing requirement.

Chemistry of heterogeneous catalysts reported, includes metal hydroxides, metal complexes, metal oxides such as calcium oxide, magnesium oxide, zeolites and supported catalysts. These types of catalysts have been investigated as solid catalysts which overcome some of the drawback on use of homogeneous catalysts.

In this study, heterogeneous solid catalysts, barium oxide are used to convert the raw material into biodiesel. The raw materials used are palm oil and methanol.

1.3 RESEARCH OBJECTIVES

The objectives of this research are:

- a) To determine the conversion of palm oil using barium oxide as catalyst.
- b) To identify the optimum operating condition for the reaction.

1.4 SCOPE OF RESEARCH

The scope has been identified for this study in order to achieve the objectives. The scopes of research are listed as below:

1. Study the effect of molar ratio of methanol to oil
2. Study the effect of concentration of barium oxide.
3. Study the effect of temperature.

1.5 SIGNIFICANCE OF STUDY

The rationales and significances of this study are:

1. Creating a new technology development for the production of biodiesel.
2. Utilized unrefined oils as raw material to produce high quality biodiesel.
3. Heterogeneous catalyst as environmental friendly due to less waste production because the availability of reusing the catalyst.

CHAPTER TWO

LITERATURE REVIEW

2.1 INTRODUCTION

Doubtless, history will describe our time as the oil-based society. Nature took 500 million years to accumulate the world's oil. A century ago the oil exploitation began, first as a source of energy and now as a source both energy and raw material. Now, contemporary society is highly dependent on the oil supply for energy, transportation, food production, and in general, industrial production. Experts agree that the world's petroleum will be consumed in two centuries (Kerr, 1998). The inexorable production peak is estimated to occur sometime between 2010 and 2020, and then the oil resources will be drastically reduced at the end of this century (Campbell *et al.*, 1998). Shortly after the production peak, the more expensive fuel sources as hard-to-extract oil deposits, tarry sands, and synfuels from coal will be brought to the front of production.

In addition to the expected development and implementation of new technologies for conventional processes, such as cracking, hydrogenation, isomerization, alkylation, and including transesterification and esterification. Biofuels, the renewable fuels are arguably one of the best options to lead the transition away from petroleum fuels in the near-term and have made a recent resurgence in response to rising oil prices. However, biofuels present resource and environmental challenges depending on where, how, and from which feedstocks they are developed.

2.2 TRANSESTERIFICATION

Transesterification is one of the classic organic reactions that have enjoyed numerous laboratory uses and industrial applications. Organic chemists make use of this reaction quite as a convenient means to prepared esters. On some occasions, transesterification is more advantageous than the ester synthesis from carboxylic acids and alcohols. For instance, some carboxylic acids are sparingly soluble in organic solvents and accordingly difficult to subject to homogenous esterification whereas esters are commonly soluble in most of organic solvents. The ester-to-ester transformation is particularly useful when the parent carboxylic acids are labile and difficult to isolate. Some esters, especially methyl and ethyl esters, are readily or commercially available and thus they serve conveniently as starting materials in transesterification. This reaction can be conducted under anhydrous conditions to allow employment of moisture-sensitive materials. Transesterification is applicable not only to the pure organic synthesis but also to polymerization as example, ring opening of lactones. Besides the laboratory utilization, transesterification has long history in industry as well. Production of esters of oils and fats is very important and transesterification processes were shown to have worked early in this century. Transesterification also plays a central role in the paint industry such as curing of alkyd resins. In the middle of this century, the reaction between dimethyl terephthalate and ethylene glycol became a crucial step for polyester production although the process has almost been replaced by direct esterification of terephthalic acid today.

Transesterification is a process where an ester is transformed into another through interchange of the alkoxy moiety (Figure 2.1). Since the reaction is an equilibrium process, the transformation occurs essentially by simply mixing the two components.

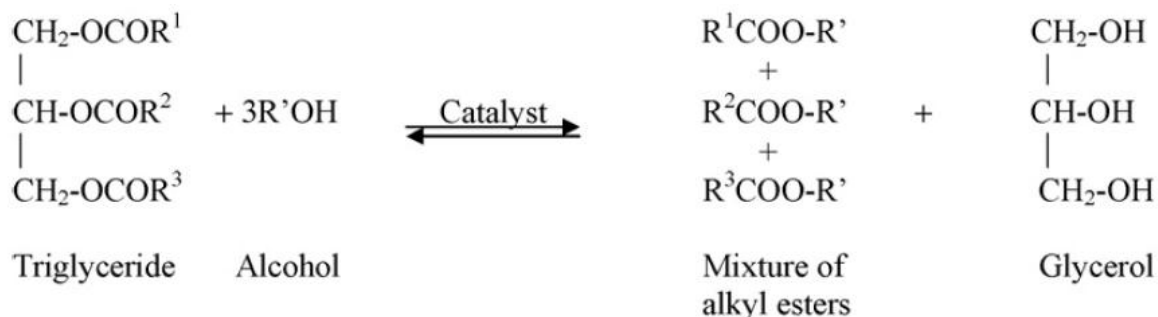


Figure 2.1: Transesterification equation

However, it has been known that the reaction is accelerated by acid or base catalysts. Because of their versatility, the acid- or base- catalyzed reactions were the subjects of extensive investigation, and the fundamental features were almost brought to light during 1950s and 1960s.

Rajesh *et al.*, (2009) said that catalysis of the transesterification reaction can be broadly classified into two categories-chemical and enzymatic. Chemically, transesterification reaction can be acid/base catalyzed. The mixture of oil with excess of ethanol when refluxed at 70°C for 1 h gave ethyl esters of fatty acids with a yield of 93%. Though the yield is high, the process has many disadvantages such as high energy consumption, difficulty in the transesterification of triglycerides with high free fatty acid content.

Georgogianni *et al.* (2009) in comparisons of homogeneous and heterogeneous catalysis in transesterification process said that homogeneous catalyst significantly accelerated the transesterification reaction using both mechanical stirring and ultrasonication. However, the use of homogeneous base catalysts requires neutralization and separation from the reaction mixture leading to a series of environmental problems related to the use of high amounts of solvents and energy. Heterogeneous solid base catalysts however can be easily separated from the reaction mixture without the use of water, they are easily regenerated and have a less corrosive nature, leading to safer, cheaper and more environment-friendly operations.

2.3 METAL OXIDE CATALYST

Homogeneous catalyst are effective and feasible, but they lead to serious contamination problems that make essential the implementation of good separation and product purification protocols, resulting in increased production cost. To be economic and to complete commercially with petroleum-based diesel fuel, processes for the synthesis of biodiesel need to involve continuous processing in a flow system, have as few reaction steps as possible, limit the number of separation processes, and ideally use the potential solid catalyst for the heterogeneous transesterification reaction.

The catalyst efficiency depends on several factors such as specific area, pore size, pore volume and active site concentration. The structure of metal oxides is made up of positive metal ions (cations) which possess Lewis acidity, i.e. they behave as electron acceptors, and negative oxygen ions (anions) which behave as proton acceptors and are thus Bronsted bases. This has consequences for adsorption. In methanolysis of oils, it provides sufficient adsorptive sites for methanol, in which the (O-H) bonds readily break into methoxide anions and hydrogen cations. The methoxide anions then react with triglyceride molecules to yield methyl esters (Chorkendorff and Niemantsverdriet, 2003). Liu *et al.* (2008) found that small amounts of water can improve the catalytic activity of CaO and biodiesel yields because in the presence of water, methoxide anions can be formed from extraction of H^+ which will be the catalyst. However, if too much water (more than 2.8% by weight of oil) is added to methanol, the fatty acid methyl ester will hydrolyze to generate fatty acids, which can react with CaO to form soap. Dossin *et al.* (2006) showed that the transesterification reaction occurs between the methanol molecules adsorbed on a magnesium oxide. The methanol adsorption is assumed to be rate-determining step in catalysts such as MgO and La_2O_3 while the surface reaction step becomes rate-determining with catalysts having a higher basicity, such as BaO, CaO or SrO.

Calcium oxide is the metal oxide catalyst most frequently applied for biodiesel synthesis, probably due to its cheap price, minor toxicity and high availability. It can be synthesized from cheap sources like limestone and calcium hydroxide. Calcium oxide possesses relatively high basic strength and less environmental impacts due to its low solubility in methanol (Zabeti *et al.*, 2009).