

**PROCESS OPTIMIZATION FOR ESTERIFICATION FROM
NON-EDIBLE RUBBER SEED**

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**This thesis is submitted to Faculty of Mechanical Engineering
as a requirement to get award of
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DECLARATION

“I hereby declare that the work in this thesis is my own except for summaries and quotations which have been duly acknowledged.”

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ABSTRAK

Biodiesel sebagai sumber tenaga boleh diperbaharui adalah bahan bakar alternatif yang menarik di mana mempunyai keluaran rendah, boleh biorosot, tanpa toksik, dan juga pelincir yang lebih baik berbanding dengan bahan api fosil. Biodiesel adalah lebih selamat untuk mengawal dan menyimpan kerana takat kilat yang tinggi. Kandungan asid lemak bebas yang tinggi dalam minyak biji getah akan menyebabkan penyabunan. Oleh itu, kajian ini dijalankan dengan tujuan untuk mengoptimumkan parameter pengesteran dengan menggunakan reka bentuk eksperimen dengan minyak biji getah. Reka bentuk pusat-komposit 3-faktor 5-peringkat bergabung dengan kaedah permukaan sambutan digunakan untuk mengkaji kesan faktor-faktor pengurangan peratusan kandungan asid lemak bebas dan mengoptimumkan keadaan tindak balas. Faktor-faktor yang dipilih untuk dikaji adalah nisbah molar metanol kepada minyak, kepekatan pemangkin, dan masa tindak balas. Satu model kuadratik penuh digunakan untuk ramalan peratusan kandungan asid lemak bebas. Pekali penentuan model adalah 91.70% yang menunjukkan ketepatan model yang boleh diterima. Parameter optimum diperolehi adalah nisbah molar metanol kepada minyak sebanyak 16.7, 3.3% berat asid sulfurik pekat sebagai pemangkin, dan masa tindak balas sebanyak 50.82 minit. Sambutan optimum peratusan lemak bebas kandungan asid adalah 0.667% menggunakan parameter optimum. Proses transesterifikasi telah dijalankan dan hasil sebanyak 88.06% adalah diperolehi dengan menggunakan minyak biji getah yang telah dirawat dan paling rendah kandungan asid bebas. Nilai asid dan titik kilat biodiesel dihasilkan memenuhi spesifikasi piawaian ASTM biodiesel, hanya kelikatan kinematik sedikit melebihi had yang ditetapkan.

ABSTRACT

Biodiesel as a renewable energy source is an attractive alternative fuel which are low emissions, biodegradable, nontoxic, and also better lubricant compare to fossil fuel. Biodiesel is safer to handle and store due to its high flash point. High free fatty acid content in rubber seed oil would causes saponification. Thus, the study is conducted with the aim of optimize the esterification parameters by using design of experiment with rubber seed oil as feedstock oil. A 5-level-3-factor central-composite design coupled with response surface methodology is used to study the effect of factors on the reduction of percentage of free fatty acid content and optimizing the reaction conditions. The factors chosen for studied are molar ratio of methanol to oil, catalyst concentration, and reaction time. A full quadratic model was used for the prediction of percentage of free fatty acid content. The coefficient of determination of the model was 91.70% which indicates the acceptable accuracy of the model. The optimum parameters obtained are molar ratio of methanol to oil of 16.7, 3.3 wt% of concentrated sulphuric acid as the catalyst, and reaction time of 50.82 minutes. The optimum response of percentage of free fatty acid content was 0.667% using these optimum parameters. The transesterification process was conducted and a yield of 88.06% is obtained using the lowest free acid content pretreated rubber seed oil. The acid value and flash point of biodiesel produced met the specifications of ASTM biodiesel standards, only the kinematic viscosity slightly exceeds the upper limit of the requirement.

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LIST OF SYMBOLS

$^{\circ}\text{C}$	=	Degree Celsius
g	=	Gram
g/cm^3	=	Gram per cubic centimeter
$\text{mPa}\cdot\text{s}$	=	Millipascal second
ml	=	Millilitre
N	=	Normality
cP	=	Centipoise
g/mol	=	Gram per mole
mol/L	=	Mole per litre
T	=	Temperature
V	=	Volume
m	=	Mass
ρ	=	Density
α	=	Distance for axial runs
R^2	=	Coefficient of determination
$\%\text{FFA}$	=	Percentage of Free Fatty Acid content
$\text{wt}\%$	=	Weight percent
x	=	Mass Fraction
M_r	=	Molecular weight
x_1	=	Molar ratio of methanol to oil
x_2	=	Catalyst concentration
x_3	=	Reaction time
y	=	Percentage of free fatty acid

LIST OF ABBREVIATION

ANOVA	=	Analysis of Variance
ASTM	=	American Society for Testing and Materials
AV	=	Acid Value
BBD	=	Box-Behnken Design
CCD	=	Central Composite Design
DOE	=	Design of Experiment
FAEE	=	Fatty Acid Ethyl Ester
FAME	=	Fatty Acid Methyl Ester
FFA	=	Free Fatty Acid
FYP	=	Final Year Project
IV	=	Iodine Value
RSM	=	Response Surface Methodology
RSO	=	Rubber Seed Oil

CHAPTER 1

INTRODUCTION

1.1 BIODIESEL

The steady supply of energy is the essential part for a modern lifestyle, where people use the energy for various applications in daily activity. The major world's energy supplies are from fossil fuels and nuclear energy. Fossil fuel is the largest contributor to the transportation fuel. Energy sources can be categorized as renewable or nonrenewable energy. The fossil fuels are able to be formed naturally by the decay of the dead organisms, but the process takes over millions of years. Since traditional fossil fuel resources are being depleted and in addition, the consumption of energy is growing rapidly, the renewable energy is currently receiving increased attention (Muley, 2008).

Biodiesel as a renewable energy source is an attractive alternative fuel used to replace fossil fuel. Biodiesel is generally produced by transesterification from renewable biological sources. The major feed stocks used for production of biodiesel are edible oils such as soybeans, rapeseed, sunflower, corn, olive and palm oil. In order to provide a better food security, the non-edible oils such as Jatropha, Pongamia pinnata and tiger nut oil is used instead of edible oils (Satyanarayanareddy & Regupathi, n.d.). Low cost oils such as waste cooking oil could reduce the production cost however there is a drawback due to the presence of the high free fatty acids (FFA) content (Lam et al., 2010).

The utilization of the fossil fuels bring the negative impact to the environment which is emission of carbon dioxide and other harmful gases such as sulphur oxides, nitrogen oxides, carbon monoxide, and ash deposition (Muley, 2008). The combustion of fossil fuels produces 21.3 billion tons of carbon dioxide per year (Annual, 2007). The advantages of the biodiesel are low emissions, biodegradable, nontoxic, and also better lubricant compare to fossil fuel (Lam et al., 2010; Wan Omar & Saidina Amin, 2011). Biodiesel is safer to handle and store due to its high flash point.

The first concept of using vegetable oil as a fuel resource was in 1895. The first diesel engine that runs with vegetable oil was designed by Rudolf Diesel in 1900. In 1912, Rudolf Diesel declared that the use of vegetable oils as engine fuels may seem insignificant during that time, but he predicted that the biodiesel may become as important as petroleum and the coal tar products in the future (Ahmad et al., 2012). Vegetable oils were used as diesel fuels from time to time in the 1930s and 1940s, but usually only in emergency situations.

Further research on the other biodiesel resources, such as palm oil, soybean oil, sunflower oil, coconut oil, rapeseed oil and tung oil, has been conducted. The research on animal fats does not reach to the same extent as vegetable oils because some methods applicable to vegetable oils are not applicable to animal fats due to natural property differences. The study also has been done on other uncommon biodiesel resources, such as oil from algae, bacteria, fungi, terpenes, latexes and microalgae (Shay, 1993).

1.2 PROBLEM STATEMENT

Energy is an essential element for the development of civilizations. Fossil fuel as a non-renewable energy source is the primary and leading energy source and majorly consumed by the transport sector (Batidzirai et al., 2012). The depletion of fossil fuel resources and the increasing in fuel consumption lead to continuous rise in petroleum oil prices (Zabeti et al., 2009). Furthermore, the utilization of fossil fuels also causes degradation of environment quality (Kanwal, 2012). These have focused attention on using alternative energy sources such as biodiesel which is a renewable energy source, to replace fossil fuels as the transportation fuels.

Biodiesel is an ideal replacement for the fossil fuel as the transportation fuel. However, there is some obstacles and challenge in biodiesel production. The current cost of the biodiesel production is very high, which is 1.5 times higher than that of petroleum-based diesel production (Lin et al., 2012). Biodiesel production from edible feedstock results high production cost and food crisis, due to the demand for human consumption (Satyanarayanareddy & Regupathi, n.d.; Patil et al., 2012).

The main factor that reduces the yield of biodiesel production is the soap formation from saponification process. The high free fatty acid content in rubber seed oil would react with alkaline catalyst to produce soap during transesterification process. Soap formed would hinder the separation process and causes emulsion.

Biodiesel can be used directly in the diesel engines, but many problems arose for long term uses. The major problems are high viscosity and impurity of biodiesel fuel, which causing reduce in performance, high exhaust emissions and reduce in engine life (Tippayawong & Sittisun, 2012). The biodiesel must meet the ASTM standard for biodiesel specification for safety concern.

1.3 OBJECTIVES

The objectives of this study are:

1. To explore and examines the potential biodiesel production from non-edible Rubber Seed Oil (RSO).
2. To optimize esterification parameters by using design of experiment (DOE).
3. To analysis and compare the physical properties of biodiesel fuel with standard diesel.

1.4 SCOPES

The scopes covered in this study are:

1. Conducting experiment of biodiesel production using RSO
2. Optimization of esterification parameters using Response Surface Methodology (RSM)
3. Study factor parameters and variables effected biodiesel synthesis and esterification reaction
4. Statistical analysis and simulation using analysis of variance (ANOVA)

CHAPTER 2

LITERATURE REVIEW

2.1 METHOD OF BIODIESEL PRODUCTION

Biodiesel can be produced in four main methods, which are direct use and blending, microemulsion, thermal cracking (pyrolysis) and transesterification. Transesterification is the most common methods due to its relatively simple procedure and cost-effective production. Besides that, transesterification can also lower the viscosity of the biodiesel and produces glycerol as a by-product which has extra commercial value (Hoque & Gee, 2013).

Direct use of crude oil or direct blending of crude oil with diesel fuel is impractical due to varies problems occurred, such as high viscosity, high FFA content, gum formation, polymerization during storage and combustion, carbon deposits, and thickening of lubricating oil (Lal & Sarma, 2011). In order to overcome the major high viscosity problem, the other three methods could be carried out. Microemulsion is generally a thermodynamically stable dispersion of mixture of two normally immiscible liquids, normally water and oil (Ma & Hanna, 1999). The problems of microemulsion are carbon deposit and lubricating oil contamination. Pyrolysis is a heat treatment process which decomposes the substance with the presence of the catalyst and the absence of air or oxygen. The pyrolysis process is no waste of water and pollution free, however its equipment is expensive and the removal of oxygen during the thermal processing rule out the use of oxygenated fuel which has environmental benefits, such as complete fuel combustion and reducing harmful emissions.

2.2 CHEMISTRY IN BIODIESEL PRODUCTION

2.2.1 Chemical Formula of Feedstock Oil

All vegetable oils and animal fats consist primarily of triglyceride molecules which has the schematic configuration as shown in Figure 2.1, where R₁, R₂, and R₃ represent the hydrocarbon chains of the fatty acyl groups of the triglyceride.

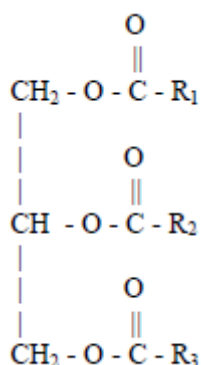


Figure 2.1: The schematic configuration of triglyceride molecules exist in vegetable oils or animal fats (Gerpen et al., 2004).

The fatty acids in free form have the configuration as shown in Figure 2.2, where R is a hydrocarbon chain equal or higher than 10 carbon atoms.

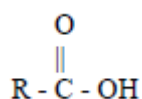


Figure 2.2: The schematic configuration of fatty acids in free form (Gerpen et al., 2004).

2.2.2 Transesterification

Transesterification is a reaction process of a triglyceride molecule with an excess of alcohol in the presence of a catalyst to produce glycerol and fatty esters (Gerpen et al., 2004). The chemical reaction of triglyceride molecule with alcohol is shown schematically as in the Figure 2.3. The reaction is reversible and hence excess alcohol is used to ensure the equilibrium shift on right hand side, which increases the yield of fatty esters (Muley, 2008).

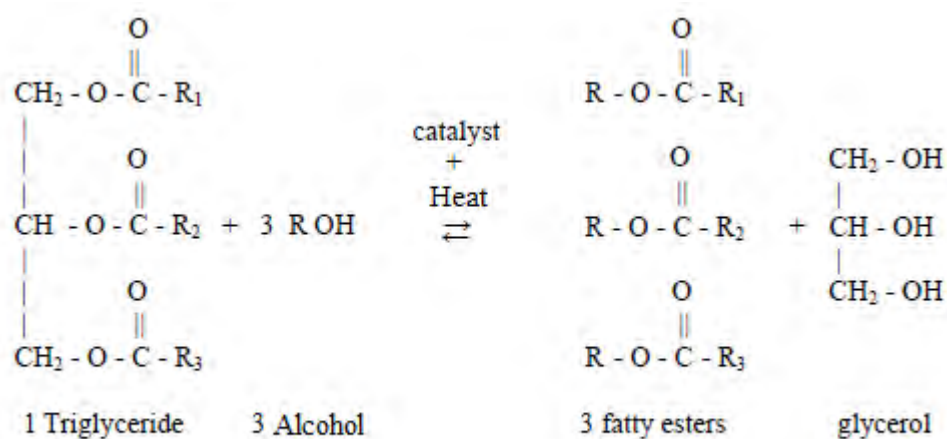


Figure 2.3: The overall chemical equation of transesterification process.

The equation shown in Figure 2.3 is an overall equation of transesterification. The actual reaction involve with 3 steps reaction as shown in Figure 2.4. First, the triglyceride reacts with alcohol to produce diglyceride and fatty ester. Then, the diglyceride reacts with alcohol to produce monoglyceride and fatty ester. Finally, the monoglyceride reacts with alcohol to produce glycerol and fatty ester.

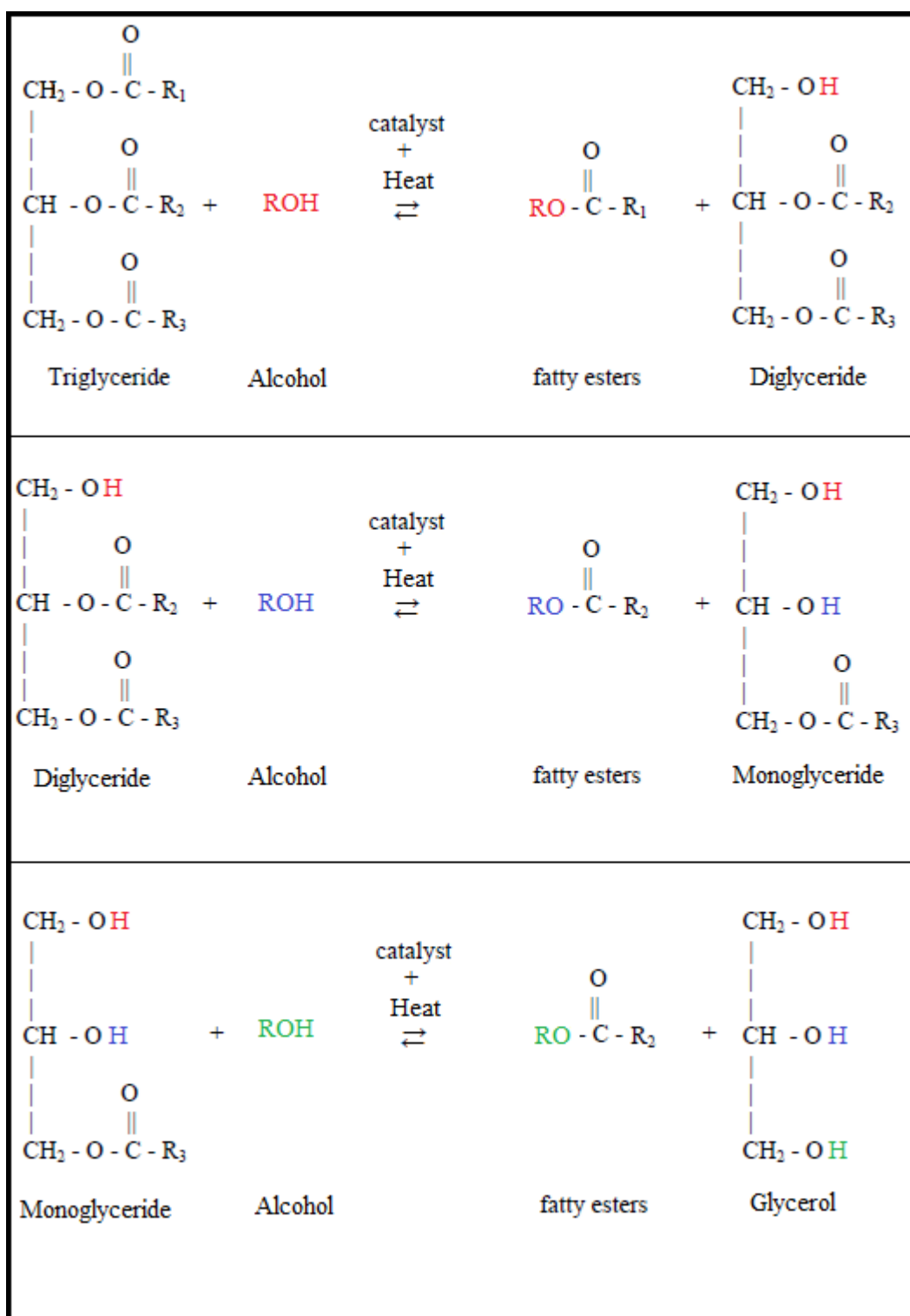


Figure 2.4: The steps involve in the transesterification reaction.

Organic fats and oils are triglycerides which are three hydrocarbon chains connected by glycerol. During the transesterification process, the bonds are broken by hydrolyzing them to form free fatty acids. These fatty acids are then mixed or reacted with methanol or ethanol forming methyl or ethyl fatty acid esters (monocarbon acid esters). The mixture separates and settles out leaving the glycerol on the bottom and the biodiesel (methyl ester, ethyl ester) on the top. In order to avoid reversed reaction, the separation of these two substances has to be conducted completely and quickly. The transesterification reactions are often conducted with the presence of acid or base catalyst (Rutz, 2008). Furthermore, if alkaline catalyst is used in transesterification process, the reactant must be free from water because water content initiate saponification. This makes the transesterification reaction partially change to saponification.

The common alcohols used in the transesterification process are mainly methanol and ethanol while higher or secondary alcohols are also available. The advantages of methanol are readily available, higher reactivity and low cost, thus it is widely used. Methanol can be obtained from renewable sources, however it is highly toxic which is a major problem. Ethanol provides better solubility for oil than methanol. It also can be obtained from renewable agricultural resources. Ethanol can produce ethyl esters with higher heat content and cetane number during transesterification process. The disadvantage is the hydrophilic nature of ethanol, having a tendency to mix with or dissolve in water, which requires proper storage (Demirbas, 2008).

The most commonly method for biodiesel production is transesterification with methanol, also called methanolysis. The solubility of methanol in vegetable oil is relatively low, so it is necessary to mix all ingredients well. The product of biodiesel yield from methanolysis is fatty acid methyl ester (FAME) (Rutz, 2008).

Ethanolysis reaction is more environmental friendly compare to methanolysis, since methanol usually is a fossil product, while ethanolysis allows the production of an entirely renewable fuel. Besides that, ethanol is much less toxic and produces biodiesel with slightly higher in heat content and cetane number. However, ethanolysis requires higher energy and has problems with the separation of the ester