Experimental Optimization of the Alkaline Catalyzed Transesterification Process for Biodiesel Production from Pre-treated Rubber Seed Oil

by

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and the original work contained herein have not been undertaken or done by unspecified sources or persons.

(YAPP HIONK YEINN)

ABSTRACT

Biodiesel is a very promising alternative fuel to the existing petroleum diesel due to its renewability and environmental friendliness. Currently, biodiesel is mostly produced from vegetable oils using alcohol and alkaline catalyst. However, most of the vegetable oils have very high content of free fatty acid (FFA) especially rubber seed oil (RSO) which requires the two-step transesterification process involving acid-catalyzed esterification process (Step 1) followed by alkaline-catalyzed transesterification process (Step 2). The acid esterification process is to reduce the FFA content to an acceptable range (< 1%) and it is usually followed by the alkaline transesterification process which is to convert the oil to methyl esters (biodiesel). In this work, the crude rubber seed oil, which is used as the feedstock, is first characterized and then the FFA content of the oil is reduced to less than 1% through the acid esterification process. The pre-treated rubber seed oil is then used for the second step of alkaline transesterification process to produce biodiesel using methanol and potassium hydroxide (KOH) as the catalyst. Experiment runs are designed and conducted to optimize the alkaline transesterification process by varying important factors such as alcohol to oil molar ratio, amount of catalyst, reaction temperature, and time. Highest yield of biodiesel (75.51 wt%) is obtained at methanol to oil ratio of 6:1, temperature of 65°C, and catalyst amount of 0.5 wt% (oil basis). It is found that the biodiesel yield is strongly affected by the catalyst amount, followed by the temperature and the alcohol to oil ratio in descending order. The effect of reaction time is also studied and the optimum reaction time is found to be at 2 hours which produces biodiesel with highest yield and FAME concentration of 96.6 wt%. The properties of the biodiesel produced at the optimal conditions and 2 hours of reaction time is found to adhere to the international standards for biodiesel (ASTM and EN).

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ABBREVIATIONS AND NOMENCLATURES

AOCS	American Oil Chemists' Society
ASTM	American Society for Testing and Materials
BS	British Standard
CFPP	Cold Filter Plugging Point
CHNS	Carbon, Hydrogen, Nitrogen, Sulfur
CP	Cloud Point
CRSO	Crude Rubber Seed Oil
EN	European Standards
FAME	Fatty Acid Methyl Esters
FFA	Free Fatty Acids
FP	Flash Point
GC	Gas Chromatography
KF	Karl Fischer
PP	Pour Point
RSO	Rubber Seed Oil

CHAPTER 1: INTRODUCTION

1.1 Background

Today, fossil fuel is the most economically available source of energy which is widely used for electricity generation, transportation, and heat production. Approximately 97% of all the transportation energy in the United States is currently produced from non-renewable petroleum fuel (David, 1998). However, fossil fuel is non-renewable and is going to deplete in few generations' time. Besides, fossil fuel also contributes a lot to the greenhouse gas problem which leads to climate change. The concern for the environmental degradation and fossil fuel depletion is rising and leads to increasing effort to develop alternatives for fossil fuels.

Biomass which also known as a collective term for all plant and animal material such as agricultural wastes and poultry excretes is becoming a very potential substitute for fossil fuel due to its renewable nature and CO_2 neutral property. Biomass can be converted into bio-fuels or liquid fuels such as biodiesel and bio-oil.

Biodiesel is a chemically modified alternative fuel which can be produced from non-edible vegetable oils, animal fats, and waste oils. These biodiesels are either in the form of triacylglycerols or *trans*-esterified with various monohydric alcohols (Klopfenstein & Walker, 1983). Vegetable oils have several benefits such as very low sulfur content, no storage complication, and great lubrication properties which make them a very good alternative to diesel fuel (Ramadhas, Jayaraj, & Muraleedharan, 2005a). Examples of vegetable oils that can be used to produce biodiesel are corn oil, canola oil, soybean oil, sunflower oil, palm oil, rubber seed oil, cotton seed oil, algae oil, and coconut oil (Mousdale, 2010).

Common methods to convert vegetable oils to biodiesel that is suitable to be used in diesel engines include blending with diesel, emulsification, pyrolysis, thermal cracking and transesterification (Ramadhas, Muraleedharan, & Jayaraj, 2005). Among the methods mentioned, transesterification of vegetable oils is more preferable because the byproduct (glycerol) of the reaction has commercial value (Ramadhas, Jayaraj et al., 2005a).

1.2 Problem Statement

Presently, most of the biodiesel is produced from the transesterification of vegetable oils process using methanol and alkaline catalyst. However, according to Ramadhas, Jayaraj et al. (2005a), there is a problem with using alkaline-catalyzed transesterification on the vegetable oils because they often have high content of free fatty acids (FFA which will react with the alkaline catalyst to form soaps through saponification which will inhibit the separation of the esterification products of ester and glycerin (Ramadhas, Jayaraj et al., 2005a). According to Ramadhas, Jayaraj et al. (2005a), the yield of biodiesel would be very low if the FFA content is more than 2%.

Thus in order to overcome the problem, a two-step transesterification process is developed in converting the high FFA oils to methyl esters (Ramadhas, Jayaraj et al., 2005a). The two-step process involves an acid catalyzed esterification followed by an alkaline catalyzed transesterification process. The first process of acid catalyzed esterification reacts and reduces the content of FFA in the oil and the second process of alkaline catalyzed transesterification process converts the products from the first step to its mono-esters (biodiesel) and glycerol (Ramadhas, Jayaraj et al., 2005a).

So in this work, the two-step transesterification process is improved by optimizing the second step which is the alkaline transesterification process (Step 2) and studying the effects of important factors such as the alcohol to oil molar ratio, catalyst amount, reaction temperature, and time on the overall yield of biodiesel. The vegetable oil that is used to produce biodiesel in this work is the rubber seed oil (RSO).

1.3 Objectives

The aims of this project are:

1. To study the effects of alcohol to oil molar ratio, catalyst amount, reaction temperature, and time on the yield of biodiesel produced from pre-treated rubber seed oil through the alkaline transesterification process (Step 2).
2. To optimize the operating conditions for the alkaline transesterification process (Step 2) by varying important factors such as the alcohol to oil molar ratio, catalyst amount, reaction temperature, and time to obtain the highest yield of the biodiesel produced.

1.4 Scope of Study

1. Characterizing the rubber seed oil in terms of its density, specific gravity, kinematic viscosity, water content, flash point, calorific value, acid value, and CHNS *elemental analysis*.
2. Pre-treating the crude RSO by reducing its free fatty acid content to less than 1% through the optimized acid esterification process (Step 1).
3. Optimizing the alkaline transesterification process (Step 2) to produce biodiesel from the pre-treated RSO with the highest yield by varying the molar ratio of alcohol to oil, amount of catalyst, reaction temperature and also time.
4. Characterizing the biodiesel produced in terms of its density, specific gravity, kinematic viscosity, water content, calorific value, flash point, cloud point, pour point, cold filter plugging point, sulphur content, acid value, and esters content.
5. Doing comparative analysis to compare the fuel properties of the biodiesel produced with international biodiesel standards (ASTM and EN) to verify its quality.

1.5 Significance of the Project

Vegetable oils especially rubber seed oils are becoming more attractive to be one of the alternative fuels to substitute petroleum diesel which is a finite and polluting source of energy. Rubber seeds are a source of non-edible oil that is cheap and abundant in Malaysia (M. Khan & Yusup, 2009). Malaysia has estimated average of 1,028,840 hectares of rubber plantation in the year 2010 (Malaysian Rubber Board, 2012). Assuming the estimated production rate of 1000 kg seeds per hectare per year, the estimated yearly production of rubber seeds in Malaysia would be around 1 million metric tons. Since Malaysia has an abundant agriculture resources like rubber seeds, it would be beneficial and a good opportunity to expand the economy of the country by improving and optimizing the method of producing biodiesel from the rubber seed oil (RSO). Besides, this work would also reduce the overall cost to produce biodiesel since the feedstock (RSO) that is used for this work is cheap and abundant in the country. Furthermore, it would be significant to improve the current method by optimizing the operating conditions to produce biodiesel at the highest yield from high FFA oils such as RSO in order to conserve energy and increase the process efficiency as sustainable development is concerned. Thus this project can ultimately help in increasing the utilization of bio-fuels as the alternative fuel to the current non-renewable petroleum diesel, creating a sustainable way of generating energy and power for the future generations.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter covers the literature review which is the analytical, critical and objective review of written materials. The literature review includes the background study and research on petroleum diesel, rubber seed oil (RSO), biodiesel, as well as the two-step transesterification process to produce biodiesel from RSO.

2.2 Petroleum Diesel

Petroleum diesel, which is a liquid fuel used in diesel engines, is produced from refined crude oil (petroleum) through processes such as crude distillation, catalytic reforming, hydrotreating, etc. Crude oil consists of a complex mixture of organic liquids, mainly hydrocarbons that are formed underground millions of years ago. Crude oil is extracted from the ground or under the sea, through oil wells, and then transported by pipeline or ship to refineries where it is processed into refined products such as fuels, lubricant oils, waxes, asphalt, and various petrochemicals.

In the process of refining, the crude oil is fractionated into liquefied petroleum gas, naphtha, kerosene, diesel oil, and residual fuel oil according to their own boiling points. The products of crude distillation are shown in **Table 2.1** according to their respective boiling points.

In crude distillation, the crude oils are first desalted and then introduced with steam to an atmospheric distillation column (Fahim, Alsahhaf, & Elkilani, 2010). Then, catalytic cracking and reforming, thermal cracking and other secondary processes are used to achieve the final desired product specifications (World Bank Group, 1999). The diesel fuel is a product resulting from the catalytic cracking of the heavy gas oil.

Table 2.1 Crude Distillation Products (Gary & Handwerk, 2001)

Products	**True Boiling Temperature (°C)**
Refinery gases (C1-C2)	-
Liquid petroleum gases (LPG)	-
Light straight run (LSR)	32-82
Heavy straight run (HSR)	82-193
Kerosene	193-271
Light gas oil (LGO)	271-321
Heavy gas oil (HGO)	321-427
Vacuum gas oil (VGO)	427-566
Vacuum residue (VR)	+566

Diesel fuel is mainly used in diesel engine which is an internal combustion engine that burns the diesel fuel to generate work. The diesel engines are commonly used as mechanical engines to produce shaft work, power generators to generate electricity, and also engines to drive cars and locomotives. They are also widely utilities in many industries like chemical process plants, construction and mining sites to provide power, mechanical works, and also to generate heat for processes. Diesel engines have several advantages over other engines because they have higher thermal efficiency and do not require sparks to ignite because they employ compression ignition instead, which results in a higher temperature in the engine.

Although petroleum diesel is one of the major sources of energy and fuel used to run engines and generate electricity, there is still concern that it is depleting due to its non-renewability. Problem of environmental degradation also arises due to the combustion of diesel fuel which releases greenhouse gases like carbon dioxide and sulfur dioxide.

2.3 Rubber Seed Oil (RSO)

Rubber seed oil is a kind of non-edible vegetable oil extracted from the rubber seed. Rubber seed is obtained in high yield as a by-product *Hevea* cultivated primarily for its latex (Aigbodion & Pillai, 2000). Research has shown that rubber seed has a very rich source of oil which makes it a potential alternative fuel for diesel engines. There is also high availability of rubber seed especially in Malaysia which has estimated average of 1,028,840 hectares of rubber plantation in the year 2010 (Malaysian Rubber Board, 2012). Assuming the estimated production rate of 1000 kg seeds per hectare per year, the projected annual production of rubber seeds in Malaysia would be around 1 million metric tons.

The rubber seed kernels contain up to 40-50% of pale yellow oil and the free fatty acid (FFA) content of unrefined rubber seed oil is about 17% (acid value of 34) (Ramadhas, Jayaraj, & Muraleedharan, 2005b). The fatty acid composition of the rubber seed oil reported by Ramadhas, Jayaraj et al. (2005b) is shown in **Table 2.2**.

Table 2.2 Fatty Acid Composition of Rubber Seed Oil (Ramadhas, Jayaraj et al., 2005b)

Fatty Acid	Composition (%)
Saturated	
$C_{16:0}$ palmitic acid	10.2
$C_{18:0}$ stearic acid	8.7
Unsaturated	
$C_{18:1}$ oleic acid	24.6
$C_{18:2}$ linoleic acid	39.6
$C_{18:3}$ linolenic acid	16.3
Others	0.6

Vegetable oils are increasingly being utilised in edible and non-edible applications which include surface coatings such as paints, printing inks, rubber/plastic processing, pharmaceuticals, lubricants, cosmetics, chemical intermediates, and diesel fuel substitute (Aigbodion & Pillai, 2000). As a result of the wide range of applications, the demand for the vegetable oils have increased and thus it is beneficial to explore the methods or processes that upgrade vegetable oils to more refined biodiesels.

From the study conducted by Ramadhas, Jayaraj et al. (2005b), where the objective was to analyze the suitability of RSO as an alternative for diesel fuel, it has been found that RSO can be directly used in engines instead of diesel fuel without any major modification done to the engine structure. However, the use of RSO in direct injection diesel engines can be restricted by the undesirable physical properties especially the viscosity, which is around 10 times higher than that of diesel (Ramadhas, Jayaraj et al., 2005a).

The characterization of RSO has also been done by Ramadhas, Jayaraj et al. (2005a) and compared with other oils such as sunflower oil, rapeseed oil, cotton seed oil and soybean oil. The characterization and comparison done by Ramadhas, Jayaraj et al. (2005a) is shown in **Table 2.3** below:

Table 2.3 Properties of Rubber Seed Oil in Comparison with Other Oils (Ramadhas, Jayaraj et al., 2005a)

Property	**Rubber seed oil**	**Sunflower oil**	**Rape seed oil**	**Cotton seed oil**	**Soybean oil**
Specific gravity	0.91	0.918	0.914	0.912	0.92
Viscosity (mm^2/s) at 40°C	66.2	58	39.5	50	65
Flash point (°C)	*198*	220	*280*	*210*	*230*
Calorific value (MJ/kg)	37.5	39.5	37.6	39.6	39.6
Acid value	34	0.15	1.14	0.11	0.2

From the properties shown in the **Table 2.3** above, it can be seen that rubber seed oil has the lowest density. However, it also has the highest viscosity, lowest flash point and calorific value, and highest acid value which are quite disadvantageous for it to be used in diesel engines. The other property data from various literatures is also compiled and shown in **Table 2.4**.

Table 2.4 Properties of Rubber Seed Oil from Various Literatures

Property	**Unit**	**A**	**B**	**C**	**D**	**E**	**F**	**G**
Specific gravity	kg/m^3	0.91	0.91	0.943	0.9182	0.922[a]	0.91[a]	0.926[a]
Viscosity at 40°C	mm^2/s	66	76.4	-	31.84	41.24[a]	-	-
Flash point	°C	198	198	-	240	294	-	-
Calorific value	MJ/kg	37.5	37.5	-	39.223		-	-
Peroxide value	meq/kg	-	-	-	-	2.5	-	0.4
Saponification value	mg KOH/g	206	206	226.12	-	194	206.20	192.93
Iodine value	g I_2/100g	-	135.3	142.45	-	142.6	135.36	155.56
Acid Value	mg KOH/g	34	53	75.38	-	4	53.09	23.00
Moisture content	wt%	-	-	-	0.108	-	-	-

[a], Tested at 30°C.

A, from (Ramadhas, Jayaraj et al., 2005a).

B, from (Ramadhas, Jayaraj et al., 2005b).

C, from (Ebewele, Iyayi, & Hymore, 2010).

D, from (Pianthong & Thaiyasuit, 2011).

E, from (Ikwuagwu, Ononogbu, & Njoku, 2000).

F, from (Aigbodion & Pillai, 2000)

G, from (Okieimen, 2000).

It is basically a necessity to reduce the viscosity of the RSO so that it can be used as a fuel in diesel engines. According to Ramadhas, Jayaraj et al. (2005a), the commonly used methods to reduce the viscosity of vegetable oils are blending with diesel, emulsification, pyrolysis, cracking and transesterification. Among these methods, transesterification is the more suitable one because the byproduct of glycerol has commercial value (Ramadhas, Jayaraj et al., 2005a).

2.4 Biodiesel

Biodiesel is a clean burning alternative fuel that is produced from domestic and renewable resources (biomass such as vegetable oils and animal oils), and it can be used pure or mixed without carrying out major changes in conventional engines (Santander et al., 2010). In contrast with petroleum diesel, biodiesel is usually produced using the conventional method through transesterification of vegetable oils using alkaline as the catalyst. In the transesterification reaction, the vegetable oil is reacted with methanol with alkaline catalyst to produce glycerol and the biodiesel is obtained in the form of esters.

Unlike petroleum diesel, biodiesel is more advantageous over petroleum diesel and it is the best substitute for petroleum diesel. One of the advantages includes its environmental friendliness because it is described as "carbon neutral" where the fuel emits zero net amount of CO_2. This is because the biomass that is used to produce biodiesel absorbs the same amount of CO_2 as is released when the fuel is combusted. Besides, biodiesel also reduces the CO_2 emission by 78% compared to petroleum diesel (Atadashi, Aroua, & Aziz, 2010). It also has higher cetane number and also higher flash point (Aigbodion & Pillai, 2000) which means that it has higher combustion quality during compression ignition and also is safer for storage compared to petroleum diesel.

Biodiesel can be blended with any proportion with mineral diesel to form a biodiesel blend or can also be used in its pure form (Agarwal, 2007). One of the applications of biodiesel is that it can be used in compression ignition diesel engines with very little or without engine modifications required due to the similar properties of the biodiesel with petroleum diesel as which can be seen in **Table 2.5**. It can also be stored in a similar way like petroleum diesel and thus it does not require any extra infrastructure or more advanced storage technologies.

The properties of RSO and biodiesel in comparison with diesel are obtained by Ramadhas, Jayaraj et al. (2005b) and Ramadhas, Muraleedharan et al. (2005), and they are shown in **Table 2.5** below:

Table 2.5 Properties of Rubber Seed Oil and Biodiesel in Comparison with Biodiesel Standard and Diesel (Ramadhas, Jayaraj et al., 2005b; Ramadhas, Muraleedharan et al., 2005)

Property	**Rubber Seed Oil**	**Biodiesel (RSO)**	**Biodiesel Standard ASTM 6751-02**	**Diesel**
Specific gravity	0.91	0.874	0.87-0.90	0.835
Viscosity (mm^2/s) at 40°C	76.4	5.81	1.9-6.0	7.50
Flash point (°C)	198	130	Min. 130	50
Calorific value (kJ/kg)	37,500	36,500	-	42,250
Saponification value (mg KOH/g)	206	-	-	-
Iodine value (g I_2/100g)	135.3	-	-	38.3
Acid value (mg KOH/g)	53.0	-	0.8	0.063

2.5 Two-Step Transesterification of Rubber Seed Oil to Produce Biodiesel

In the present days, biodiesel is mostly produced through the transesterification of vegetable oils using methanol and alkaline catalyst. Transesterification (alcoholysis) is the chemical reaction between triglycerides and alcohol in the presence of alkaline catalyst to produce methyl esters (biodiesel) and glycerin (byproduct) (Ma & Hanna, 1999; Ramadhas, Jayaraj et al., 2005a).

The transesterification process is made up of three successive reversible reactions where the triglycerides are converted to diglycerides first, followed by the conversion of diglycerides to monoglycerides, and lastly, the conversion of glycerides to glycerol and ester (Ramadhas, Jayaraj et al., 2005a). The overall transesterification reaction is shown in **Figure 2.1** below:

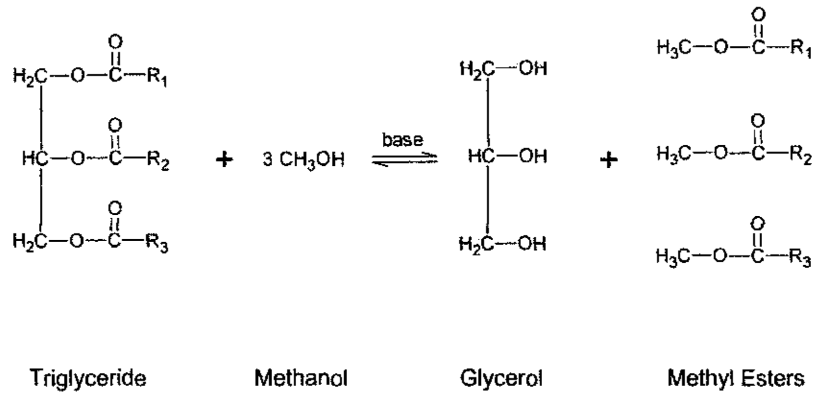

Figure 2.1 Overall Transesterification Reaction

From the reaction scheme above, it can be seen that three moles of alcohol are needed to react with one mole of triglyceride. Practically, a higher alcohol to oil molar ratio is normally used so that the equilibrium reaction is favoured to the right in order to produce more ester and increase the extend of reaction. Methanol is usually used due to its low cost and alkaline hydroxides like sodium hydroxide are also preferred because of the higher effectiveness compared to acid catalysts.

However, there is a major drawback in using alkaline as the transesterification catalyst because the alkaline will react with the free fatty acids (FFA) in vegetable oils to produce soaps that will inhibit the separation of ester and glycerin. According to Ramadhas, Jayaraj et al. (2005a), alkaline catalyzed transesterification of vegetable oils is possible only if the acid value of oil is less than 4 because a higher percentage of FFA (more than 2%) in the oil will reduce the yield of the esterification process considerably.

In order to overcome the problem of the alkaline catalyst, a two-step transesterification process is developed to convert the FFA in the vegetable oils to its mono-esters. The two-step transesterification process involves a first step of acid catalyzed esterification to reduce the content of FFA and a second step of alkaline catalyzed transesterification to convert the products from the first step to mono-esters and glycerol (as shown in **Figure 2.1**). The acid catalyzed esterification process which reacts the FFA in vegetable oils with alcohol is shown in **Figure 2.2**:

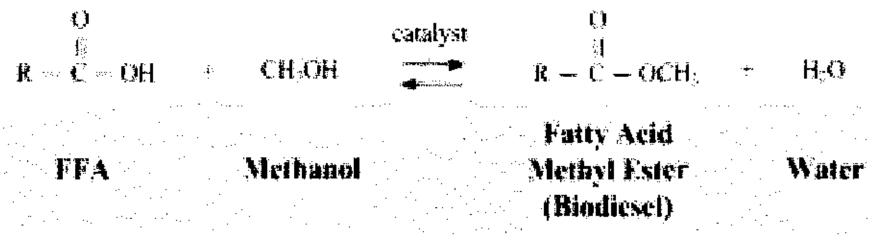

Figure 2.2 Esterification Reaction

Research has been done by Khan et al. (2010) and Yusup and Khan (2010) in analyzing the major factors that affect the conversion efficiency of the acid esterification process and alkaline transesterification respectively to produce biodiesel from blends of crude palm oil and crude rubber seed oil.

Similar study has also been done by Ramadhas, Jayaraj et al. (2005a) in determining the optimum conditions for the two-step transesterification processes of crude rubber seed oil. The factors that were considered in these studies include:

1. Molar ratio of alcohol to oil
2. Amount of catalyst
3. *Reaction temperature*
4. Reaction time
5. Mixing speed

The catalysts used in the studies are sulfuric acid as the acid catalyst and potassium hydroxide/sodium hydroxide as the alkaline catalyst. The conditions were varied in both the acid esterification process (step 1) and the alkaline transesterification process (step 2) and the variations are summarized in **Table 2.6** below:

Table 2.6 Conditions Variations of Two-step Transesterification Process (M. A. Khan, Yusup, & Ahmad, 2010; Ramadhas, Jayaraj et al., 2005a; Yusup & Khan, 2010)

Factor	**Variation Range**			
	Acid Esterification (Step 1)		**Alkaline Transesterification (Step 2)**	
	(M. A. Khan et al., 2010)	**(Ramadhas, Jayaraj et al., 2005a)**	**(Yusup & Khan, 2010)**	**(Ramadhas, Jayaraj et al., 2005a)**
Alcohol to oil molar ratio	10:1-20:1	3:1-9:1	6:1-10:1	6:1-15:1
Catalyst amount	0.5-2 wt%	0.25-2 wt%	0.5-2 wt%	0.3-1 wt%
Reaction temperature	45-65°C	40-50°C	45-65°C	40-50°C
Reaction duration	3 hours	30 mins	3 hours	30 mins
Mixing speed	6 Hz	-	6 Hz	-

For reaction duration of 3 hours, it is found that a molar ratio of 15:1 at 65°C with 0.5 wt% of H_2SO_4 favours the completion of acid catalyzed esterification process (M. A. Khan et al., 2010) and a molar ratio of 8:1 at 55°C with 2 wt% of KOH favours the completion of alkaline catalyzed transesterification process (Yusup & Khan, 2010) with constant mixing rate of 6 Hz for blends of crude palm oil and crude rubber seed oil.

On the other hand, for shorter reaction duration of 30 minutes, lower alcohol to oil ratio of 6:1 and lower temperature of 40-50°C favours the acid esterification process, and alcohol to oil ratio of 9:1, a much lower amount of catalyst (0.5 wt% NaOH) and lower temperature of 40-50°C favours the alkaline transesterification process of crude rubber seed oil (Ramadhas, Jayaraj et al., 2005a). The optimum conditions for both steps are summarized in **Table 2.7**.

Table 2.7 Optimum Conditions of Two-step Transesterification Process (M. A. Khan et al., 2010; Ramadhas, Jayaraj et al., 2005a; Yusup & Khan, 2010)

Factor	**Optimum Conditions**			
	Acid Esterification (Step 1)		**Alkaline Transesterification (Step 2)**	
	(M. A. Khan et al., 2010)	**(Ramadhas, Jayaraj et al., 2005a)**	**(Yusup & Khan, 2010)**	**(Ramadhas, Jayaraj et al., 2005a)**
Alcohol to oil molar ratio	15:1	6:1	8:1	9:1
Catalyst amount	0.5 wt% H_2SO_4	0.5 wt% H_2SO_4	2 wt% KOH	0.5 wt% NaOH
Reaction temperature	65°C	40-50°C	55°C	40-50°C
Reaction duration	3 hours	30 mins	3 hours	30 mins
Mixing speed	6 Hz	-	6 Hz	-

From the results obtained by Khan et al. (2010), the biodiesel obtained through the acid esterification (step 1) using the optimum conditions in **Table 2.7** has the lowest value of FFA percentage, which is a mean value of 0.541%. The temperature had the highest effect over the FFA reduction followed by alcohol amount while the catalyst had the lowest effect (M. A. Khan et al., 2010).

For the alkaline transesterification step, the optimum conditions were based on the highest conversion of the methyl esters in the biodiesel which was recorded at more than 96 wt% (Yusup & Khan, 2010). The biodiesel conversion favoured high temperatures and catalyst amount and also lower alcohol amount in order to control the soap formation and product losses (Yusup & Khan, 2010). The optimum temperature is preferred not to be too high (>65°C) because the methanol would vaporise and escape from the system.

The biodiesel produced by Yusup and Khan (2010) was compared with both ASTM 6751 and EN 14214 biodiesel standards and the biodiesel produced by Ramadhas, Jayaraj et al. (2005a) is compared with ASTM 6751-02 biodiesel standard and also the properties of other biodiesels of different feedstock. It was proven that the biodiesels are suitable to be used as commercial substitute for diesel fuel. It is also proven that this two-step transesterification method can reduce the overall cost of production of biodiesel because it uses low cost unrefined non-edible oils (Ramadhas, Jayaraj et al., 2005a).

The data such as the density and molar mass of methanol, vegetable oil (rubber seed oil), glycerol, and biodiesel which are the reactants and products of the two-step transesterification process is shown in **Table 2.8**.

Table 2.8 Data for the Reactants and Products of the Two-Step Transesterification Process (Austin Peay State University, n.d.)

Reference Data	Density (g/mL)	Molar Mass (g/mol)
Methanol	0.7918	32.04
Vegetable Oil	0.915	872
Glycerol	1.26	92.9
Biodiesel	0.88	292.2

CHAPTER 3: METHODOLOGY

3.1 Introduction

The methodology of this project covers the experimental works which include characterization of rubber seed oil, rubber seed oil pre-treating (Step 1), experimental *optimization of alkaline transesterification for biodiesel production* (Step 2), and also property testing methods to verify the biodiesel quality. This chapter discusses on the project research methodology, methods used for property analysis, experimental procedures for Step 1 and Step 2, tools and chemicals needed for the experiments, as well as the Gantt chart for FYP 2.

3.2 Research Methodology

3.2.1 1st Stage: Project Planning

The problem related to the project is identified and the significance of the project is also determined. The objective and also scope of study are outlined and the feasibility of the project work is ensured to be within the time frame given. The solution to the problem statement is studied and the types of materials and tools used for the experiment are also identified through literature review.

3.2.2 2nd Stage: Characterization of Rubber Seed Oil

The rubber seed oil used for the experiment is characterized first. The properties which are analyzed include the density, specific gravity, kinematic viscosity, water content, flash point, calorific value, and acid value. The crude rubber seed oil that is used in this work is from Vietnam and obtained through oil extraction using n-hexane.

3.2.3 3rd Stage: Screening and Identification

The types of alcohol and catalysts to produce biodiesel from the rubber seed oil are identified. The suitable range of conditions or variables for the esterification processes are also identified and screened through literature review. The variables that will affect the conversion and yield of biodiesel from RSO include the alcohol to oil molar ratio, amount of catalyst, reaction temperature, and time.

3.2.4 4th Stage: Experimental Design and Works

The equipment setup for the experiments is determined. The equipment and also chemicals required for the experiments are identified with a clear experimental procedure outlined and planned. The equipment and methods needed to analyze the properties of samples are also identified. After that, the experimental works will be conducted in the laboratory to obtain the data and results.

3.2.5 5th Stage: Comparative Study

The conversion and yield of the biodiesel obtained using different conditions are determined and analyzed using gas chromatography (GC) and then comparative study is done to obtain the optimum conditions for the alkaline transesterification process. The experiment is then repeated at the optimum conditions. The biodiesel produced is then characterized and compared with international standards like ASTM and EN to verify its quality.

The flowchart that summarizes the research methodology is shown in **Figure 3.1** below:

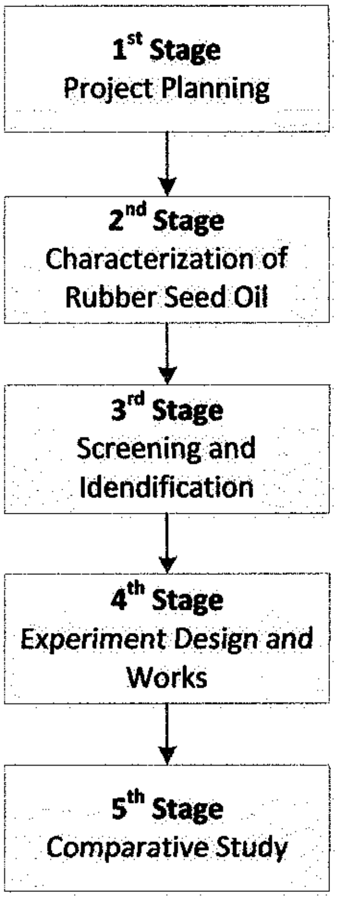

Figure 3.1 Research Methodology Flowchart

3.3 Analysis

Before the experiments are started, the rubber seed oil needs to be characterized to determine its characteristics and properties. The biodiesels that are produced needs to be characterized and analyzed for its properties too to be compared with international biodiesel standards to verify their qualities and also for other comparative studies. The property analysis covers:

1. Density
2. Kinematic Viscosity
3. Water Content
4. Calorific value
5. Flash Point (FP)
6. Cloud Point (CP)
7. Pour Point (PP)
8. Cold Filter Plugging Point (CFPP)
9. CHNS analysis
10. Acid Value (FFA Content)
11. Fatty Acid Methyl Esters (FAME) Content

3.3.1 Density

The density measurement is carried out using the Anton Paar DMA 4500 M Density Meter in accordance with the testing method of ASTM D4052. The temperature of the density meter is set to be at 20°C. A sample of around 2mL is prepared and then injected into the density meter's inlet nozzle using a syringe. The readings for the density and specific gravity of the sample are displayed on the panel. The procedure is repeated again to get an average value of the density.

3.3.2 Kinematic Viscosity

The kinematic viscosity of the sample is determined using the Bohlin Gemini 2 rotational rheometer manufactured by Malvern in accordance with the testing method of ASTM D445.

3.3.3 *Water Content*

The Karl Fischer (KF) titration method which is in accordance with the ASTM D6304 method is used to determine the water content using the Metrohm 831 KF Coulometer. The Karl Fischer method utilizes quantitative reaction of water with iodine in the presences of lower alcohol. The amount of iodine consumed is used to measure the water content of the sample. The sample is prepared in a syringe and its initial weight is taken. A few drops of sample are injected into the titrator and the weight is measured again to obtain the weight difference. After the weight is keyed into the operating software, the equipment will run and the water content of the sample is determined. The procedure is repeated again to get an average value of the water content.

3.3.4 Calorific Value

The calorific value of the sample is determined using the IKA® C5000 Bomb Calorimeter. Around 0.5 g of sample size is used and the calorimeter will run and determine the calorific value of the sample in accordance with the testing method of ASTM D240.

3.3.5 Flash Point

The Petrotest® Cleveland Open Cup Instrument (CLA 5) automated flash point analyzer is used to determine the ASTM D92 Flash Point of the samples.

3.3.6 Cloud Point & Pour Point

The ISL CPP 5Gs analyzer is used to determine the cloud point and pour point through the testing methods of ASTM D2500 and ASTM D97 respectively.

3.3.7 Cold Filter Plugging Point (CFPP)

The ISL FPP 5Gs analyzer is used to determine the cold filter plugging point (CFPP) in accordance with the testing method of ASTM D6371.

3.3.8 CHNS Elemental Analysis

The elemental analysis (Carbon Hydrogen Nitrogen Sulfur) is done using the LECO CHNS-932 instrument with approval of the ASTM D5291 method. Around 1.5 – 2.0 mg of sample is weighted and prepared in an aluminum container prior to the analysis. The sample is then analyzed by the analyzer and the compositions of C, H, N, and S are displayed in percentage value. The oxygen content is calculated as the remaining of the composition.

3.3.9 Acid Value (FFA Content)

The acid value is determined through the titration of potassium hydroxide (KOH) based on the official method of AOCS (Cd 3d-63) (AOCS) (Darnoko & Cheryan, 2000) used for low values of acid value.

3.3.10 Fatty Acid Methyl Esters (FAME) Content

The FAME contents of the biodiesel are determined using the Shimadzu GC-2010 Gas Chromatography with FID, based on the British standard method BS EN 14103:2003 (European Standard for Biodiesel, 2003). The areas under the peaks are identified accordingly and the FAME content is calculated using the provided equation in the British standard method.

3.4 Experimental Procedures for Producing Biodiesel from Rubber Seed Oil through Two-Step Transesterification Method

The procedures to produce biodiesel from RSO using the two-step transesterification method are divided into two major steps, which are the acid esterification process (Step 1) followed by the alkaline transesterification process (Step 2). The main purpose of Step 1 is to reduce the FFA content of the RSO to less than 1% before proceeding to Step 2 which is to convert the oil to biodiesel. Experimental optimization is done for the Step 2 to produce biodiesel with the highest yield.

3.4.1 Acid Esterification (Step 1: Rubber seed oil pre-treatment)

1. The crude rubber seed oil is first pre-treated through acid esterification to reduce the FFA content in the RSO to less than 1% in order to prevent soap formation in the next step. The acid esterification process is done at the optimum conditions obtained from previous studies as shown in **Table 3.1**:

Table 3.1 Optimum Conditions for the Acid Esterification Process (Step 1)

Parameters	Value
Methanol to oil ratio	13:1
Temperature	65°C
Catalyst amount (H_2SO_4)	10 wt%
Stirring rate	350 rpm
Reaction duration	90 minutes

2. *500 g of rubber seed oil is weighed and transferred into the three-neck round* bottom flask placed on a hot plate and heated to 65°C.
3. The flask is connected to a condenser to avoid loss of alcohol.
4. Meanwhile, a mixture of methanol (alcohol to oil molar ratio 13:1) and sulfuric acid catalyst (10 wt% of the oil) is prepared.
5. The mixture is added into the flask with RSO to start the reaction.

6. When the temperature of the mixture has become constant at 65°C, the reaction is started and the stirring rate is set at 350 rpm for 90 minutes.
7. The product mixture is then left to cool down for 15 minutes and transferred to a separating funnel for the separating stage.
8. The mixture is left to separate in a separating funnel for 24 hours.
9. The bottom phase which consists of deionized water containing glycerol, excess alcohol and catalyst (H_2SO_4) is removed.
10. The upper layer consisting of pre-treated oil is washed using warm water for several times to get rid of any used catalyst and byproducts.
11. The pre-treated RSO is then analyzed for its FFA content.
12. If the FFA content is still higher than 1%, the steps above are repeated until the FFA content is less than 1%.
13. The pre-treated RSO (FFA content < 1%) is then used for the next step (Step 2) to produce biodiesel through alkaline transesterification.

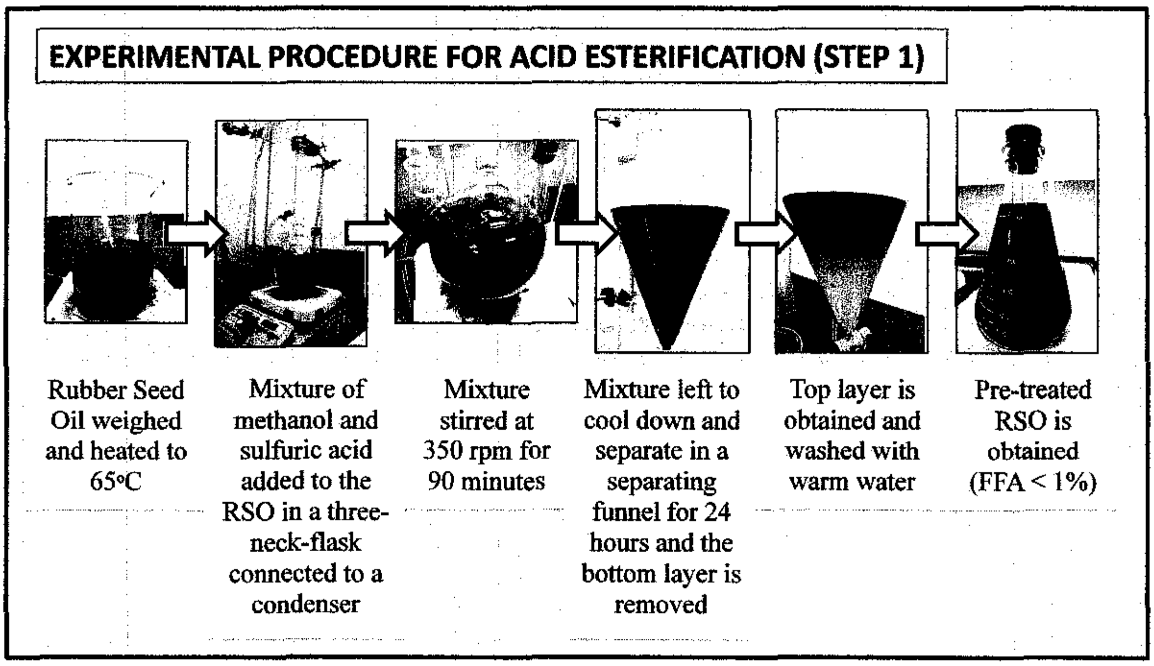

Figure 3.2 Experimental Procedure Flowchart for Acid Esterification (Step 1)

The parameters and also the calculations that are involved in the acid esterification procedure (Step 1) are shown below:

Table 3.2 Parameters for Step 1

Parameters	**Value**
Weight of RSO	500 g
Molecular weight of RSO	872 g/mol
Alcohol to oil ratio	13:1
H_2SO_4 (catalyst) amount	10 wt% of oil
Stirring rate	350 rpm
Reaction duration	90 minutes

Moles of RSO $= \dfrac{500g}{872g/mol} = 0.5734mol$

Moles of methanol needed $= \dfrac{13}{1} \times 0.5734mol = 7.454mol$

Volume of methanol needed $\dfrac{7.454mol \times 32.04g/mol}{0.792g/mL} = \underline{301.55mL}$

Weight of H_2SO_4 needed $= 0.10 \times 500g = \underline{50g}$

3.4.2 Alkaline Transesterification (Step 2: Experimental optimization of alkaline transesterification for biodiesel production)

1. Approximately 50 g of the pre-treated RSO (from Step 1) is weighed and transferred into the three-neck round bottom flask placed in a water bath on a hot plate.
2. The flask is connected to a condenser to avoid loss of alcohol.
3. The RSO is then heated to the desired temperature (45 - 55°C) in the water bath using hot plate.
4. Meanwhile, a mixture of methanol (alcohol to oil molar ratio 6:1 – 10:1) and potassium hydroxide catalyst (0.5 - 2 wt% of the oil) is prepared (according to **Table 3.3**).
5. The mixture is added into the flask with pre-treated RSO to start the second step of alkaline catalyzed transesterification (Step 2) which is to produce biodiesel from the pre-treated RSO.
6. When the mixture has reached its desired temperature, the reaction is started and the stirring rate is set at 350 rpm for 120 minutes.
7. The product mixture is then left to cool down for around 15 minutes and transferred to a separating funnel for the separation stage.
8. The mixture is left to separate in a separating funnel for 24 hours.
9. The bottom phase which consists of deionized water containing glycerol, excess alcohol and catalyst (KOH) is removed and weighed.
10. The upper layer (ester-rich phase) which consists of produced oil is washed using warm water for several times to get rid of any used catalyst and byproducts.
11. Methanol and water that might still present in the ester-rich phase are removed using the rotary evaporator with the operating conditions of 50 rpm rotation speed and temperature of 80°C at atmospheric pressure for 30 minutes.

12. Approximately 20 wt% of $Na_2S_2O_3 \cdot 5H_2O$ is added to the ester-rich phase to absorb and remove any remaining water content. The $Na_2S_2O_3 \cdot 5H_2O$ is then removed from the mixture through filtration and the biodiesel obtained is weighed.
13. The ester (FAME) content of the biodiesel is determined using gas chromatography (GC), based on the British standard method BS EN 14103:2003 (European Standard for Biodiesel, 2003).
14. The conversion, yield and selectivity of the biodiesel are then calculated.
15. Steps 1 to 14 are repeated using different alcohol to oil molar ratio, catalyst amount, and reaction temperature according to **Table 3.3** until the 9 runs are done.
16. The optimum conditions for the alkaline transesterification process (Step 2) are obtained from the analysis of the biodiesel conversion and yield for each run.
17. The optimum run obtained from Step 16 is repeated again to verify the result.
18. The effect of time is then studied by varying the reaction time (0.5-2.5 hours) using the optimum conditions to obtain the optimal reaction time.
19. The biodiesel is then characterized and compared with international biodiesel standards to verify its quality.

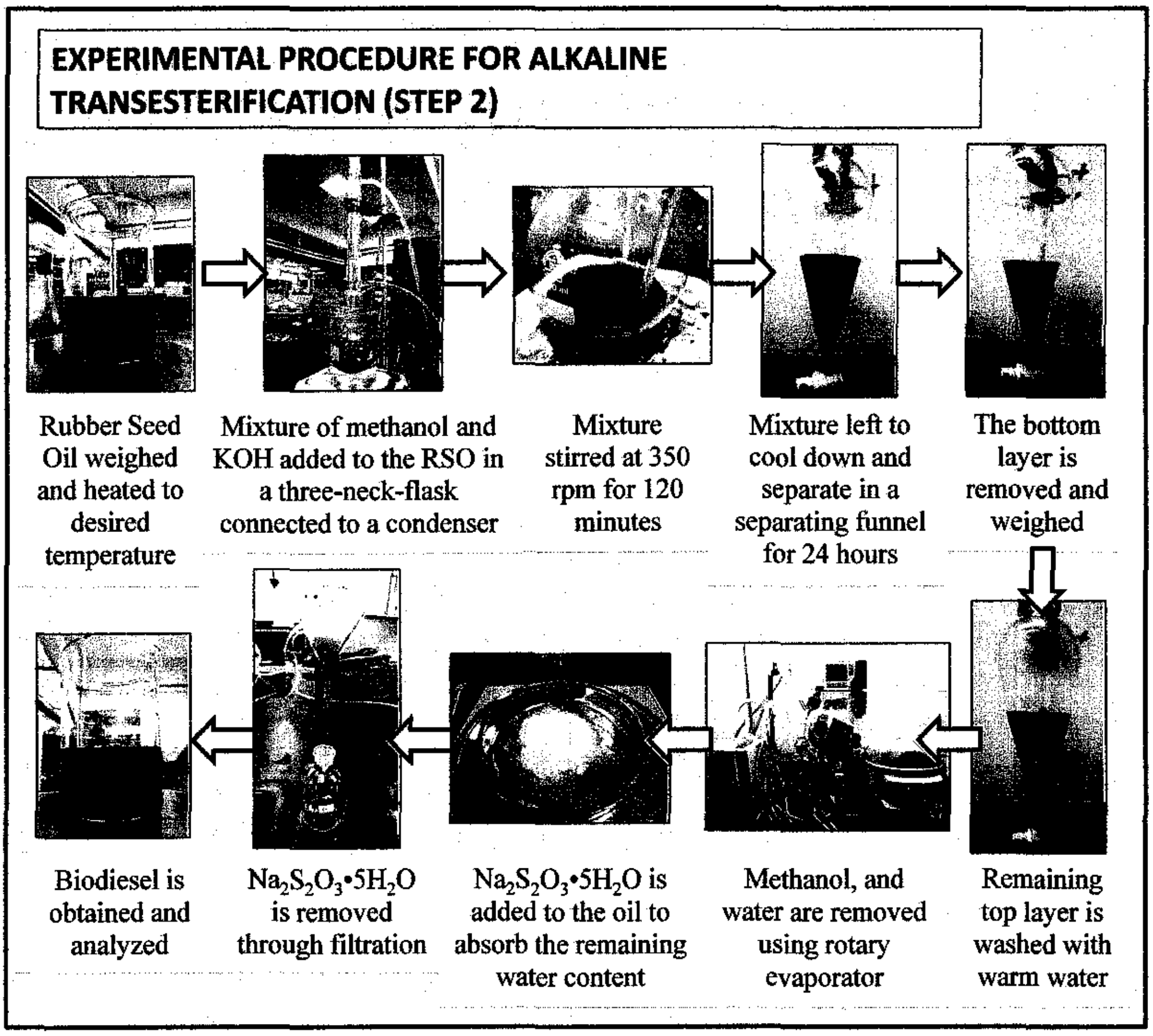

Figure 3.3 Experimental Procedure Flowchart for Alkaline Transesterification (Step 2)

The standard L9 orthogonal array was selected and used to design the experiment runs using the Taguchi method. **Table 3.3** shows the parameters and their variations that are designed and used in conducting the experiments.

Table 3.3 Alkaline Transesterification Process Variables

Run	Alcohol to Oil Molar Ratio	Temperature (°C)	Catalyst (KOH) amount (wt%)	Reaction time (mins)	Mixing Speed (rpm)
1	8:1	45	1	120	350
2	8:1	65	0.5		
3	6:1	45	0.5		
4	6:1	55	1		
5	8:1	55	2		
6	10:1	45	2		
7	10:1	65	1		
8	10:1	55	0.5		
9	6:1	65	2		

The parameters and also the calculations that are involved in the alkaline transesterification procedure (Step 2) are shown below. **Run 1** from **Table 3.3** is demonstrated as an example:

Table 3.4 Parameters for Step 2 (Run 1)

Parameters	Value
Weight of pre-treated RSO	50.08 g
Molecular weight of pre-treated RSO	872 g/mol
Alcohol to oil ratio	8:1
KOH (catalyst) amount	1 wt% of oil
Stirring rate	350 rpm
Reaction duration	120 minutes

$$\text{Moles of RSO } = \frac{50.08g}{872g/mol} = 0.0574mol$$

$$\text{Moles of methanol needed} = \frac{8}{1} \times 0.0574mol = 0.459mol$$

$$\text{Volume of methanol needed } \frac{0.459mol \times 32.04g/mol}{0.792g/mL} = \underline{18.59mL}$$

$$\text{Weight of KOH needed} = 0.01 \times 50.08g = \underline{0.5008g}$$

3.5 Process Flowchart for the Experimental Procedures

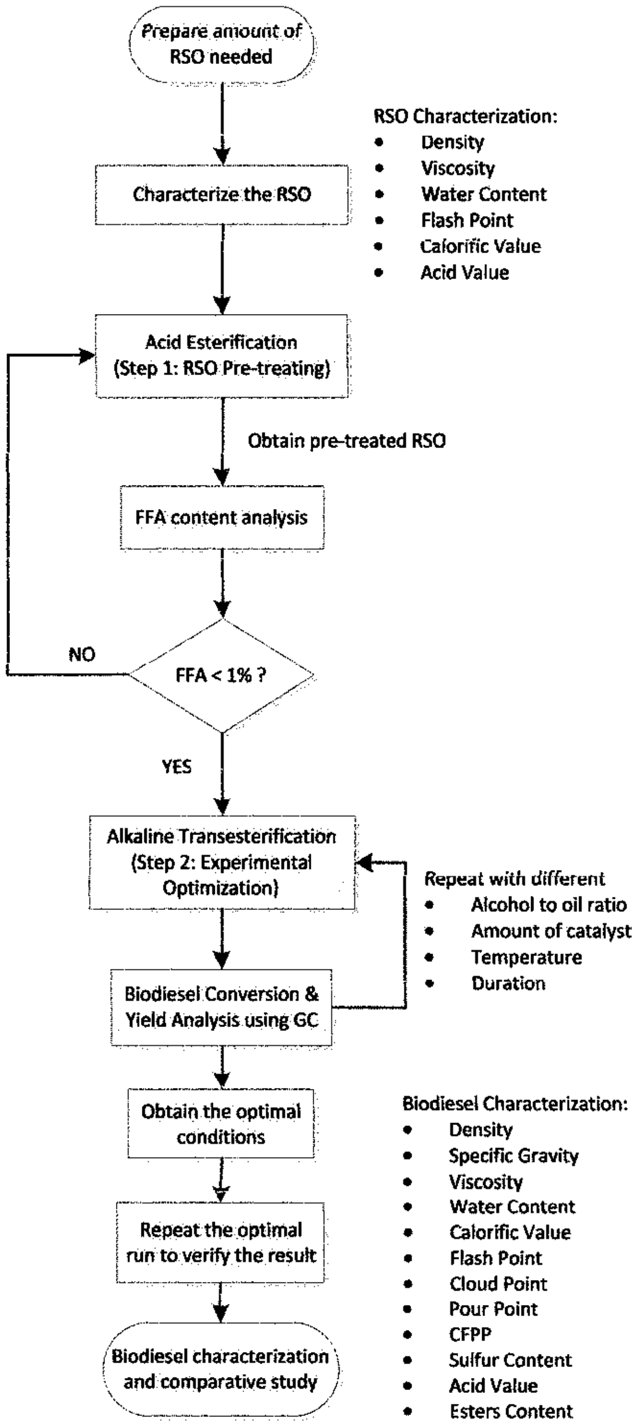

Figure 3.4 Process Flowchart of the Experimental Procedures

3.6 Tools for Experiment

1. Rotary evaporator (consists of water bath as temperature controller, vacuum pump and distillation column).
2. Three-neck round bottom flask (equipped with thermometer, magnetic stirrer, and condenser).
3. Hot plate with magnetic stirrer
4. Separating funnel
5. Conical funnel
6. Anton Paar DMA 4500 M Density Meter
7. IKA® C5000 Bomb Calorimeter
8. Bohlin Gemini 2 Rotational Rheometer
9. Metrohm 831 KF Coulometer
10. Petrotest® Cleveland Open Cup Instrument (CLA 5) automated flash point analyzer
11. ISL CPP 5Gs Cloud Point & Pour Point Analyzer
12. ISL FPP 5Gs CFPP Analyzer
13. Shimadzu GC-2010 Gas Chromatography with FID
14. LECO CHNS-932 Instrument
15. Design-Expert 8 software

3.7 Chemicals for Experiment

1. Rubber Seed Oil (From Vietnam)
2. Methanol (CH_3OH)
3. Sulfuric Acid (H_2SO_4)
4. Potassium Hydroxide (KOH)
5. Sodium thiosulfate pentrahydrate ($Na_2S_2O_3{\cdot}5H_2O$)

3.8 Gantt Chart for FYP 2

Table 3.5 Gantt Chart for FYP 2

No.	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14	15
1	RSO Pre-treating	■	■	■					Mid-semester Break							Hari Raya Break	
2	Optimization of Alkaline Transesterification Process				■	■	■	■									
3	Submission of Progress Report									■							
4	Characterization of Biodiesel									■	■	■	■				
5	Pre-SEDEX												■				
6	Submission of Draft Report												■				
7	Submission of Dissertation (Soft bounds)													■			
8	Submission of Technical Paper														■		
9	Oral Presentation																■
10	Submission of Dissertation (Hard bounds)																■

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1 Characterization of Rubber Seed Oil

The crude rubber seed oil used in this work is from Vietnam and obtained through oil extraction using n-hexane. The oil appears to be brown in color. It is characterized by analyzing its properties such as density, specific gravity, kinematic viscosity, water content, flash point, calorific value, and acid value. The results of the analysis are shown in **Table 4.1**.

Table 4.1 Results for the Characterization of Rubber Seed Oil

Property	Unit	Testing Method	Value
Density (at 15°C)	kg/m^3	ASTM D4052	915.71
Specific Gravity (at 15°C)	-	ASTM D4052	0.91736
Kinematic Viscosity (at 40°C)	mm^2/s	ASTM D445	42
Water Content	Volume %	ASTM D6304	0.98
Flash Point (open cup)	°C	ASTM D92	162.1
Calorific Value	MJ/kg	ASTM D240	37.917
Acid Value	mg KOH/g	AOCS (Cd 3d-63)	85

4.2 Acid Esterification (Step 1: Rubber Seed Oil Refining)

Before producing biodiesel from the crude rubber seed oil, the FFA content of the crude RSO needs to be reduced to less than 1% to prevent soap formation in the alkaline transesterification process (Step 2) which will complicate the separation of the desired product. The FFA content is reduced through the acid esterification process (Step 1). The acid esterification process is done on six batches of crude RSO (approximately 500 g each batch). Thus around 3 kg of pre-treated RSO is produced for the project. The FFA contents are determined through the AOCS official method (Cd 3d-63) (AOCS) (Darnoko & Cheryan, 2000) of KOH titration before and after the acid esterification process and the results from the analysis are shown in **Table 4.2**.

Table 4.2 Results for Acid Esterification Process (Step 1)

	Before Acid Esterification			After Acid Esterification		
	Trial 1	Trial 2	Average FFA%	Trial 1	Trial 2	Average FFA%
Batch 1	-	-	42.5	0.814	0.746	0.780
Batch 2				0.873	0.833	0.853
Batch 3				0.853	0.840	0.847
Batch 4				0.770	0.750	0.760
Batch 5				0.901	0.920	0.911
Batch 6				0.850	0.780	0.815
				Total average		0.828

From the results obtained, it is observed that the crude rubber seed oil has an initial FFA content of 42.5% and it is reduced to an average value of 0.828% using optimum conditions for the acid esterification process in one step. The pre-treated RSO which has FFA content of less than 1% also does not cause the problem of soap formation in the next step of alkaline transesterification.

Thus the pre-treated RSO produced from the acid esterification process at methanol to oil molar ratio of 13:1, temperature of 65°C, and catalyst amount of 10 wt% is acceptable and suitable to be used in the alkaline transesterification process to produce biodiesel.

4.3 Alkaline Transesterification (Step 2: Experimental optimization of alkaline transesterification for biodiesel production)

Following the standard L9 orthogonal array outlined in **Table 3.3**, the experiments are done according to the process variables set beforehand. The weights of the reactants used and the products obtained are shown in **Table 4.3**.

Table 4.3 Reactants and Products for Alkaline Transesterification Process

Run	Process Variables			Reactants			Products	
	Alcohol to Oil Molar Ratio	Temp. (°C)	Catalyst Amount (wt%)	RSO weight (g)	Methanol weight (g)	KOH weight (g)	Top Layer (Ester Rich Phase) (g)	Bottom Layer (Glycerol) (g)
1	8:1	45	1	50.08	14.72	0.50	33.90	10.17
2	8:1	65	0.5	50.32	14.79	0.25	37.62	8.43
3	6:1	45	0.5	49.30	10.87	0.25	33.09	12.71
4	6:1	55	1	49.72	10.96	0.50	34.49	11.52
5	8:1	55	2	50.28	14.78	1.00	18.06	33.21
6	10:1	45	2	49.89	18.33	1.00	14.74	35.35
7	10:1	65	1	50.35	18.50	0.50	35.40	11.93
8	10:1	55	0.5	50.61	18.60	0.25	40.50	8.25
9	6:1	65	2	50.29	11.09	1.00	22.02	24.35

The fatty acid methyl esters (FAME) concentration in weight percentage (wt%) of the top layer obtained for each run were analyzed using GC and the results are shown in **Table 4.4**. Then the conversion, yield and selectivity of the main product (FAME) are calculated using the following equations:

$$\textbf{Conversion (wt\%)} = \frac{(FAMEConcentration \times TopLayer) + BottomLayer}{RSO} \times 100\%$$

$$\textbf{Yield (wt\%)} = \frac{(FAMEConcentration \times TopLayer)}{RSO} \times 100\%$$

$$\textbf{Selectivity (wt\%)} = \frac{Yield}{Conversion}$$

$$= \frac{(FAMEConcentration \times TopLayer)}{(FAMEConcentration \times TopLayer) + BottomLayer} \times 100\%$$

Table 4.4 Conversion, Yield and Selectivity of FAME for Alkaline Transesterification Process

Run	Process Variables			Experimental Results			
	Alcohol to Oil Molar Ratio	**Temperature (°C)**	**Catalyst Amount (wt%)**	**FAME Concentration (wt%)**	**Conversion (wt%)**	**Yield (wt%)**	**Selectivity (wt%)**
1	8:1	45	1	93.1	83.36	63.05	75.64
2	8:1	65	0.5	91.0	84.79	68.04	80.24
3	6:1	45	0.5	91.5	87.17	61.39	70.43
4	6:1	55	1	93.4	87.97	64.80	73.66
5	8:1	55	2	92.2	99.15	33.10	33.38
6	10:1	45	2	92.5	98.19	27.34	27.84
7	10:1	65	1	90.8	87.52	63.83	72.93
8	10:1	55	0.5	91.8	89.77	73.46	81.84
9	6:1	65	2	92.3	88.85	40.43	45.51

From the results obtained, it can be seen that the FAME concentrations for all the conditions are rather high, at the range of above 90%. The yield of biodiesel is used as the criteria to determine the optimum conditions. The highest biodiesel (FAME) yield is found in Run 8, which has biodiesel yield of 73.46 wt%. Thus for the nine runs of experiments, the highest biodiesel yield for the alkaline transesterification process was found to be at alcohol to oil molar ratio of 10:1, temperature 55°C, catalyst amount of 0.5 wt%, reaction duration of 2 hours (120 minutes), and stirring rate of 350 rpm as shown in **Figure 4.1**.

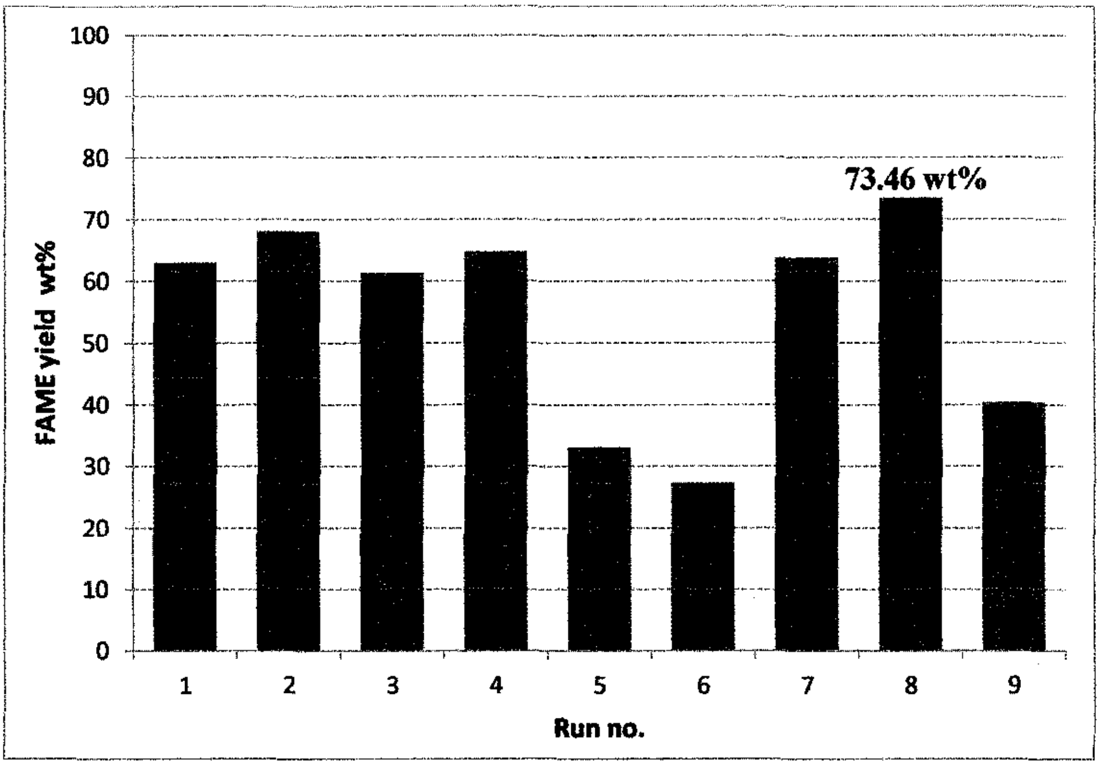

Figure 4.1 FAME (Biodiesel) Yield for Different Conditions of Alkaline Transesterification Process

However, the Run 8 which has the highest yield of biodiesel does not necessary be the optimum conditions because not all levels and variations of the factors are done since the L9 orthogonal array was used to design the experiments which is to reduce the number runs. The other results for different factors combinations are predicted using the Design-Expert 8 software. The effects of factors such as alcohol to oil ratio, catalyst amount and the temperature are also studied using the software and these are further discussed in the following sections.

4.3.1 Effect of Alcohol to Oil Molar Ratio

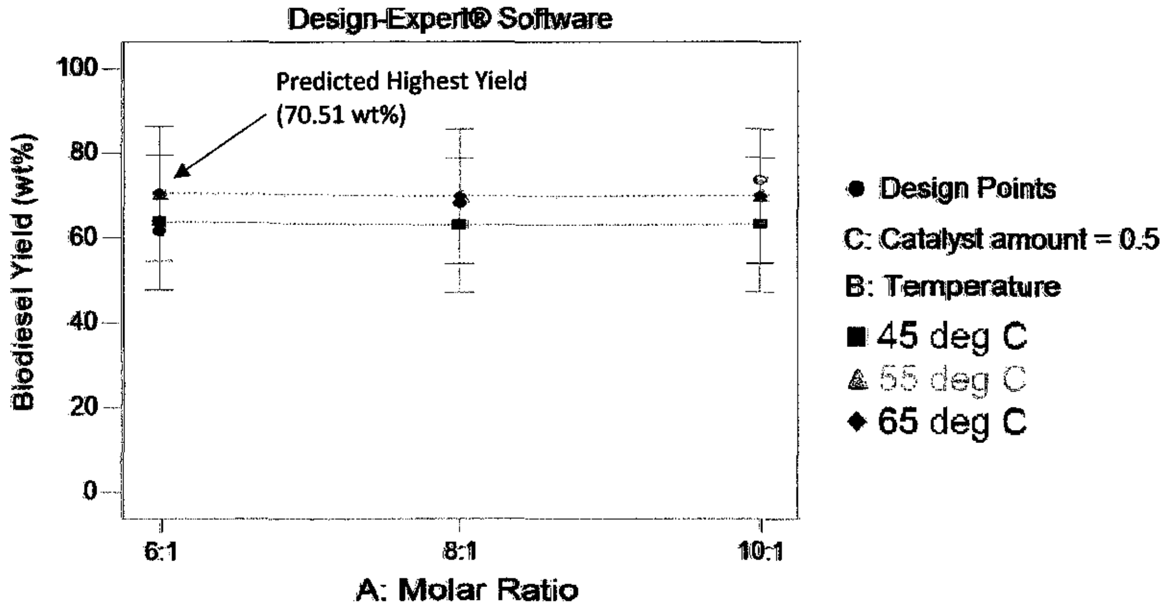

Figure 4.2 Effect of Alcohol to Oil Molar Ratio on the Yield of Biodiesel

The alcohol to oil molar ratio is the ratio of the moles of alcohol over the moles of vegetable oil used. Stoichiometrically, according to the transesterification reaction shown in **Figure 2.1**, three moles of alcohol are needed for one mole of oil (alcohol:oil ratio = 3:1) in order for the reaction to proceed. However, the amount of alcohol needed practically is higher than the stoichiometric ratio in order for the reaction to proceed to completion. Excess alcohol means higher production cost of biodiesel. Thus the molar ratio of alcohol to oil is an important factor that can affect the overall yield of biodiesel and also the overall cost to produce biodiesel.

In the experiment, the effect of alcohol to oil molar ratio on the biodiesel yield is shown in **Figure 4.2**. The ratio is varied at 6:1, 8:1, and 10:1. It is observed that the predicted maximum biodiesel yield of 70.51 wt% is achieved for the lowest molar ratio of 6:1 at 65°C and 0.5 wt% catalyst. It is also observed that the effect of alcohol to oil ratio is not that much as compared to other factors. It would be very beneficial for low alcohol to oil ratio requirement as it will reduce the cost of producing biodiesel too.

4.3.2 Effect of Temperature

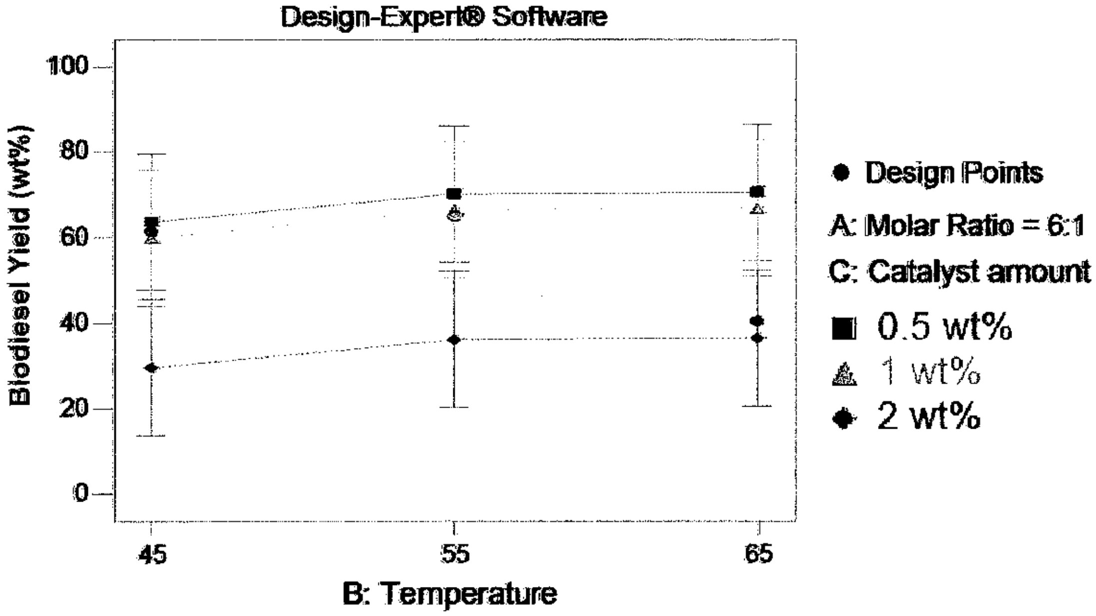

Figure 4.3 Effect of Temperature on the Biodiesel Yield

The effect of temperature on the biodiesel yield is shown in **Figure 4.3** where the increase in the reaction temperature increases the biodiesel yield until 55°C and a slight increase of biodiesel yield is observed when the temperature is at 65°C. The predicted maximum yield of biodiesel is obtained at temperature of 65°C at alcohol to oil molar ratio of 6:1 and 0.5 wt% catalyst. The optimum temperature for alkaline transesterification for the palm oil and rubber seed oil blend as reported by Yusup & Khan (2010) is at 55°C while a lower temperature range of 40-50°C is reported by Ramadhas, Jayaraj et al. (2005a) as the optimum temperatures for alkaline transesterification of RSO. However, it is advised to avoid reaction temperature higher than 60°C when RSO is used as the feedstock because it will accelerate the soap formation between the glycerides and alkaline catalyst through saponification (Ramadhas, Jayaraj et al., 2005a). Higher reaction temperature will also cause wastage of methanol in this case because methanol vaporizes at 65°C, unless higher boiling point alcohol such as butanol is being used. Thus, in order to prevent alcohol loss, condenser is connected to the reactor in order to condense and recycle back the methanol that vaporizes.

4.3.3 Effect of Catalyst Amount

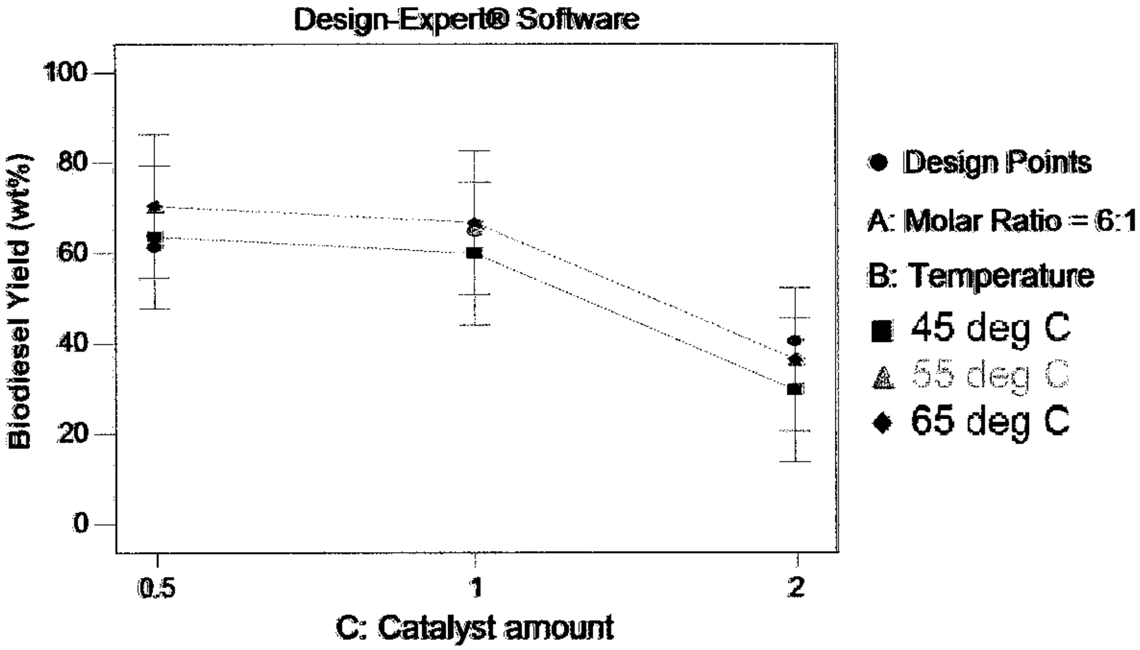

Figure 4.4 Effect of Catalyst Amount on the Biodiesel Yield

The concentration of the alkaline catalyst (potassium hydroxide, KOH) is varied from 0.5 to 1 wt% in terms of the RSO's weight. The effect of the catalyst amount on the biodiesel yield is shown in **Figure 4.4**. It is observed that increase in the catalyst amount decreases the biodiesel yield. The maximum yield of biodiesel is reported at the lowest catalyst concentration which is 0.5 wt%. Same optimum catalyst concentration (0.5 wt%) is also reported by Ramadhas, Jayaraj et al. (2005a) with a shorter reaction time of 30 minutes only.

Besides, the amount of catalyst also affects the color of the biodiesel produced. From **Figure 4.5**, it is observed that the higher the catalyst amount, the lighter the biodiesel color will be (light yellow) and low catalyst amount produces biodiesel with a darker color (brownish orange).

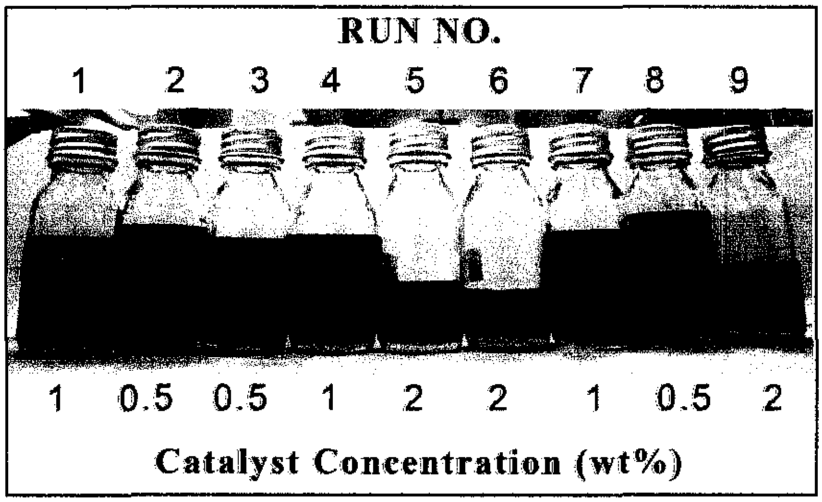

Figure 4.5 Effect of Catalyst Amount on the Biodiesel Color

4.3.4 Predicted and Experimental Optimum Conditions

From the analysis done using the Design-Expert 8 software, it is found that the new predicted optimum conditions that give the highest predicted biodiesel yield of 70.51 wt% are at alcohol to oil molar ratio of 6:1, temperature of 65°C, and catalyst amount of 0.5 wt%. In order to verify the predicted optimum conditions, the experiment is repeated at the predicted optimum conditions to obtain the experimental value of the biodiesel yield. The summary of the predicted and experimental optimum conditions is shown in **Table 4.5**.

Table 4.5 Predicted and Experimental Optimum Conditions

	Predicted Yield	**Experimental Yield**
Experimental Optimum Conditions (Run 8) **(10:1 ratio, 55°C, 0.5 wt% catalyst)**	69.53 wt%	73.46 wt%
Predicted Optimum Conditions **(6:1 ratio, 65°C, 0.5 wt% catalyst)**	70.51 wt%	75.51 wt%

The experimental biodiesel yield at the predicted optimum conditions are found to be 75.51 wt% which is higher than the biodiesel yield obtained from Run 8. Thus the new optimum conditions are verified and it can be concluded that the optimum conditions for the alkaline transesterification process (Step 2) for this work are at alcohol to oil molar ratio of 6:1, temperature of 65°C, and catalyst amount of 0.5 wt%.

4.3.5 Effect of Reaction Time

Apart from the effects of the three factors (alcohol to oil molar ratio, temperature and catalyst amount) being investigated for the alkaline transesterification, the effect of *reaction time is also studied separately to further optimize the results obtained before* this. The optimum conditions for the alkaline transesterification from the previous section are used and maintained for a certain period of time while the products are withdrawn from the system at a certain time interval (0.5, 1.0, 1.5, 2.0, and 2.5 hours). The FAME concentration for each sample product is analyzed using the GC and the FAME yield is calculated using the formula stated is **Section 4.3**. The results for the FAME yield analysis are shown in **Table 4.6**.

Table 4.6 Results of the Study on the Effect of Time for the Alkaline Transesterification Process

Reaction Time (hour(s))	RSO Weight (g)	Experimental Results		
		Top Layer Weight (g)	FAME Concentration (wt%)	FAME Yield (wt%)
0	-	-	30.7	30.70
0.5	50.83	19.43	80.3	38.22
1.0	50.03	29.80	85.5	50.93
1.5	50.10	25.81	87.9	58.30
2.0	50.58	39.52	96.6	75.51
2.5	50.30	35.64	96.6	68.45

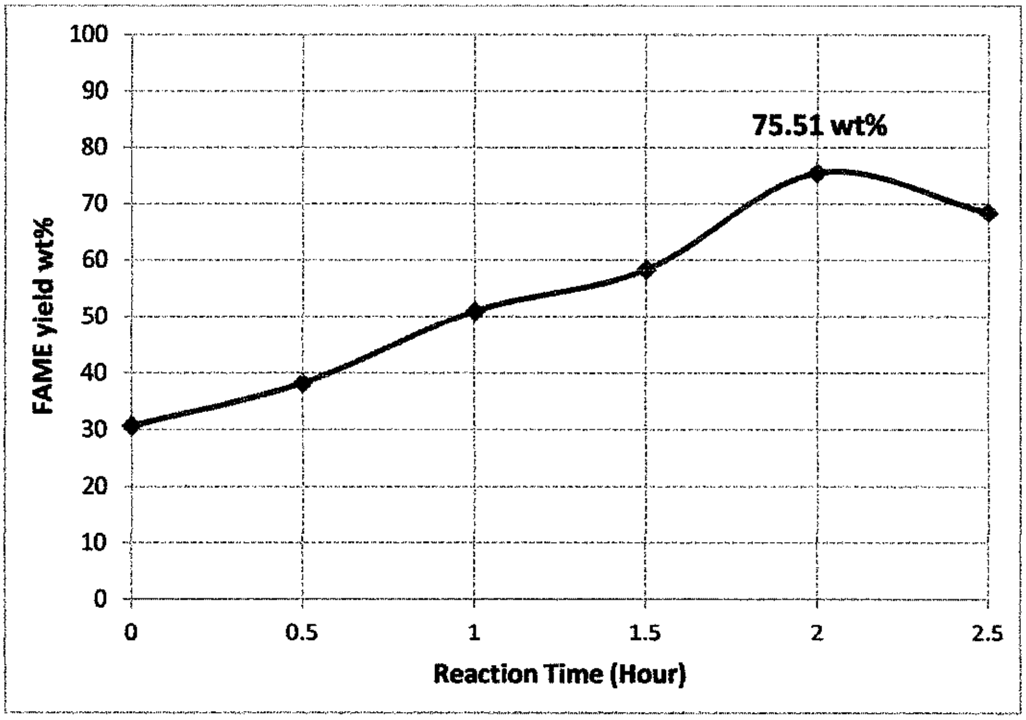

Figure 4.6 Effect of Reaction Time on the Biodiesel Yield

From the results of the FAME yield which are plotted against reaction time as shown in **Figure 4.6**, it can be noted that the FAME yield does not start from zero because some of the fatty acids may have been converted into methyl esters (FAME) during the acid esterification process (Step 1) before the alkaline transesterification process (Step 2). In this case, the pre-treated rubber seed oil contains around 30.7 wt% of FAME which is also the initial biodiesel yield for the alkaline transesterification reaction.

The FAME yield increases as the reaction continues for 2 hours and a slight drop in the yield is noticed at duration of 2.5 hours. Highest yield of FAME at around 75.51 wt% is obtained for reaction duration of 2 hours. On the other hand, the FAME concentration vs. reaction time is also plotted and shown in **Figure 4.7**.

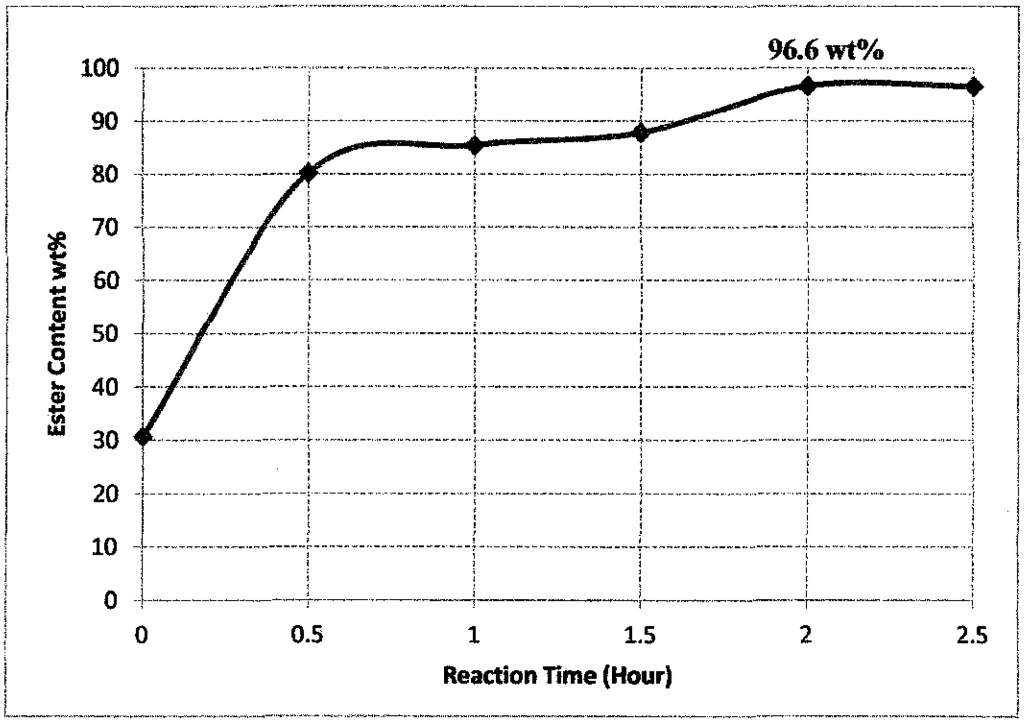

Figure 4.7 Effect of Reaction Time on the Ester Content of the Biodiesel

The FAME concentration increases drastically at the beginning of the reaction and it reaches the maximum value of 96.6 wt% at reaction time of 2 hours. The FAME concentration remains constant at 96.6 wt% when the reaction continues for another 30 minutes until reaction time of 2.5 hours is reached. Thus it can be concluded that the optimum reaction duration for the alkaline transesterification process is 2 hours where highest FAME yield and concentration are achieved.

4.4 Biodiesel Quality

The biodiesel that is produced at the optimum conditions and reaction duration of 2 hours for the alkaline transesterification is characterized and compared with ASTM and EN standards to verify its quality. The properties that are analyzed include the density, specific gravity, kinematic viscosity, water content, calorific value, flash point, cloud point, pour point, cold filter plugging point (CFPP), sulphur content, acid value, and esters content. The results for the property analysis and tests conducted on the biodiesel are shown in **Table 4.7**.

Table 4.7 Properties of Biodiesel Produced Compared with International Standards

Property	Testing Method	Unit	Value	ASTM Criteria	EN Criteria
Density (at 15°C)	ASTM D4052	kg/m^3	884.99	N/A	860-900
Specific Gravity (at 15°C)	ASTM D4052	-	0.8866	N/A	N/A
Kinematic Viscosity (at 40°C)	ASTM D445	mm^2/s	3.997	1.96-6.0	3.5-5.0
Water Content	ASTM D6304	Volume %	0.0421	Max. 0.05	Max. 0.05
Calorific Value	ASTM D240	MJ/kg	40.297	N/A	N/A
Flash Point (open cup)	ASTM D92	°C	130.2	Min. 130	Min. 120
Cloud Point	ASTM D2500	°C	3.1	-13 to 12	N/A
Pour Point	ASTM D97	°C	1.0	-15 to 10	N/A
Cold Filter Plugging Point	ASTM D6371	°C	-2.9	N/A	N/A
Sulfur Content	ASTM D5291	Weight %	0	Max. 0.05	Max. 0.1
Acid Value	AOCS (Cd 3d-63)	mg KOH/g	0.48	Max. 0.8	Max. 0.5
Esters Content	EN 14103	Weight %	96.6	N/A	Min. 96.5

From the comparison of the property analysis in **Table 4.7**, it is observed that the biodiesel produced at the optimum conditions and 2 hours of reaction duration met most of the requirements set by the international standards for biodiesel (ASTM and EN). The calorific value of the biodiesel is also quite high, around 40.297 MJ/kg, which is near to the calorific value of the diesel. Thus the biodiesel produced in this work is suitable to be used as an alternative to substitute diesel fuel in its applications.

4.5 CHNS Elemental Analysis

The elemental analysis of CHNS is also done on the crude rubber seed oil, pre-treated rubber seed oil and also the biodiesel produced from alkaline transesterification. The results of the analysis are shown in **Table 4.8**.

Table 4.8 Results for the CHNS Elemental Analysis

Sample	**Element Composition (wt%)**				
	C	**H**	**N**	**O**	**S**
Crude Rubber Seed Oil	76.520	10.390	0.298	12.792	0
Pre-treated Rubber Seed Oil	77.225	11.795	0.252	10.728	0
Biodiesel	77.145	10.032	0.315	12.508	0

From the analysis results in **Table 4.8**, all the samples do not have any content of sulphur. As reported by Ramadhas, Jayaraj et al. (2005a), vegetable oils normally have very low sulphur content. Since the sulphur content of the feedstock used in this work has zero sulphur content, the biodiesel produced from it also contains zero sulphur, which makes it more environmental friendly to be used as fuel since it also agrees to the sulphur content limit set by ASTM and EN.

CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

Vegetable oils especially rubber seed oils are becoming more attractive to be one of the alternative fuels to substitute petroleum diesel which is a finite and polluting source of energy. In Malaysia, rubber seeds are a cheap and abundant source of non-edible oil and there is estimated production rate of 1 million tons annually in the country due to the large plantation area of rubber trees. Thus it would be beneficial and a good opportunity to expand the economy of the country and also to promote and encourage the application of bio-fuels to substitute fossil fuels by producing biodiesel from the rubber seed oil (RSO).

Biodiesel is mostly produced from the vegetable oils through the transesterification process using methanol and an alkaline catalyst. However, there is a major drawback in using alkaline as the transesterification catalyst because the alkaline will react with the free fatty acids (FFA) in vegetable oils to produce soaps that will inhibit the separation of ester and glycerin. Thus the two-step transesterification process which consists of acid esterification (Step 1) followed by alkaline transesterification (Step 2) is developed to overcome the problem. The acid esterification process is to reduce the FFA content to an acceptable range (< 1%) and it is usually followed by the alkaline transesterification process which is to convert the oil to methyl esters (biodiesel).

Thus it would be significant to improve the current method with optimized conditions to produce biodiesel from cheap feedstock especially vegetable oil with high FFA content such as rubber seed oil due to its lower overall production cost and especially when sustainable development is concerned. By optimizing the process to produce biodiesel, the energy and feedstock requirements can be decreased and the efficiency of the process would be increased in overall. Crude rubber seed oil which is from Vietnam and obtained through oil extraction using n-hexane is used as the feedstock for this study. Methanol and potassium hydroxide are used as the reactant and catalyst respectively for the alkaline transesterification process.

In this work, the effects of the alcohol to oil ratio, amount of catalyst, and the reaction temperature are analyzed in the alkaline transesterification step. In order to optimize the alkaline transesterification conditions, the standard L9 orthogonal array was selected and used to design the experiment runs using the Taguchi method. The reactions are carried out for 2 hours with constant mixing speed of 350 rpm. The yield of biodiesel is used as the criteria to determine the optimum conditions. The maximum yield of biodiesel (75.51 wt%) is obtained at alcohol to oil molar ratio of 6:1, temperature 65°C, catalyst amount of 0.5 wt%. It is found that the biodiesel yield is strongly affected by the catalyst amount, followed by the temperature and the alcohol to oil ratio in descending order. It is also observed that excess addition of the alkaline catalyst lightens the color of the biodiesel. Lower amount of catalyst on the other hand produces biodiesel with darker color. The effect of the reaction time is also studied and it is found that 2 hours is the optimum reaction time which produces highest yield of biodiesel with the highest FAME concentration of 96.6 wt%. The properties of the biodiesel produced at the optimal conditions and 2 hours of reaction time is found to adhere to the international standards for biodiesel (ASTM and EN). Thus the biodiesel produced in this work is suitable to be used as an alternative to substitute diesel fuel in its applications.

In conclusion, this project can ultimately help in increasing the utilization of bio-fuels as the alternative fuel to the current non-renewable petroleum diesel, creating a sustainable way of generating energy and power. By having a good method with optimum conditions to produce biodiesel from cheap feedstock, it would help promote more research and studies being done on the method, and hopefully in the future, biodiesel would become easier and cheaper to produce and eventually substitute fossil fuels as the main source of energy.

There are also a few recommendations that are suggested to improve the project in the future. One of them is to conduct the experiments with more variation of the conditions to increase the accuracy of the results in determining the optimum conditions for the method. Another recommendation is to repeat each run of experiment for two times or more to obtain more consistent and precise results. Different feedstock can also be used to obtain different results so that comparative studies can be done among the different feedstock.

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