UNIVERSITI TEKNOLOGI MARA

TREATMENT OF FREE FATTY ACID IN SLUDGE PALM OIL VIA GLYCEROLYSIS FOR BIODIESEL FEEDSTOCK

FARAH NASYITAH BINTI ESA

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FARAH NASYITAH BINTI ESA

Thesis submitted in fulfilment
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CONFIRMATION BY PANEL OF EXAMINERS

I certify that a Panel of Examiners has met on 24 November 2025 to conduct the final examination of Farah Nasyitah Esa on her Masters of Science thesis entitled "Treatment of Free Fatty Acid in Sludge Palm Oil Via Glycerolysis for Biodiesel Feedstock" in accordance with Universiti Teknologi MARA Act 1976 (Akta 173). The Panel of Examiner recommends that the student be awarded the relevant degree. The Panel of Examiners was as follows:

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ABSTRACT

The depletion of fossil fuels has prompted the nation to transition toward sustainable and renewable energy sources. Biodiesel, which is typically produced from fats derived from vegetable oils, is one of the promising alternatives due to its notable attributes. However, the use of these oils as biodiesel feedstock has resulted in high production costs and raised concerns regarding food security. Sludge palm oil (SPO), which is primarily collected from palm oil mill effluent (POME), has the potential to replace vegetable oils as biodiesel feedstock. Nevertheless, the high free fatty acid (FFA) content in SPO is undesirable, as it causes soap formation, resulting in low biodiesel yield. Therefore, in this study, SPO was treated using the glycerolysis method to reduce the FFA content to below 3% prior to biodiesel production. SPO collected from POME was characterized both physically (FFA, moisture content, and saponification value) and chemically (functional groups, fatty acid composition, and chemical composition) to assess its feasibility as a biodiesel feedstock. A comparison between SPO and crude palm oil (CPO) was conducted, and the results indicated that both possessed similar qualities, although SPO required pretreatment. Glycerolysis was then carried out to treat SPO by adding glycerol in the presence of zinc oxide as a catalyst to reduce the FFA content (59%) through the formation of glycerides and water. The effects of reaction temperature (170°C, 190°C, and 220°C), catalyst loading (0.25 wt%, 0.50 wt%, and 1.0 wt%), and SPO to glycerol molar ratio (1:1, 1:1.5, and 1:2) on FFA reduction were investigated to determine the optimum conditions. The lowest FFA value achieved was 0.46%, corresponding to a 99.4% FFA reduction efficiency, at 220°C, 1.0 wt% catalyst loading, and a 1:2 SPO to glycerol molar ratio. The treated SPO with the lowest FFA content was subsequently used for biodiesel production via transesterification. Ethanol was employed as the alcohol, with potassium hydroxide serving as the catalyst. The produced biodiesel was analyzed using Fourier-transform infrared spectroscopy (FTIR) and gas chromatography–mass spectrometry (GC–MS) to confirm biodiesel formation. The formation of palmitic acid ethyl ester as the major composition in produced biodiesel indicated the successful conversion of SPO into biodiesel, signifying the effectiveness of glycerolysis as treatment method to reduce the FFA content in SPO.

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Abbreviations

BD	Biodiesel
CPO	Crude Palm Oil
DAG	Diglyceride
FAEE	Fatty Acid Ethyl Ester
FFA	Free Fatty Acid
FTIR	Fourier Transform Infrared Spectroscopy
GC-MS	Gas Chromatography-Mass Spectrometry
GHG	Greenhouse Gas
KOH	Potassium Hydroxide
MAG	Monoglyceride
MPOB	Malaysian Palm Oil Board
PD	Petroleum Diesel
POME	Palm Oil Milling Effluent
SDG	Sustainable Development Goals
SPO	Sludge Palm Oil
TAG	Triglyceride
ZnO	Zinc Oxide

CHAPTER 1
INTRODUCTION

1.1 Research Background

In this era of globalization, the demand of energy is increasing drastically. The constant reliance and large application of petroleum diesel as main source of energy have brought concerns to people. This is due to the depletion of this non-renewable source as well as the hazardous effects to the environment and people's health. Biodiesel is one of the effective alternatives that offers clean renewable energy, environmentally friendly approach, and limitless resources [1, 2]. Biodiesel is often defined as fatty acid alkyl ester that mainly produced from lipids originated from animal fats or vegetable oils through transesterification process. However, the main constraint on commercialising biodiesels as par as petroleum diesel is due to the high cost that mainly contributed from its raw material [3]. Other materials are being explored by researchers to obtain alternate feedstock that is low in cost, renewable and environmentally friendly.

Sludge palm oil (SPO) is an ideal alternative to replace vegetable oils and animal fats as the feedstock for biodiesel production. SPO is mainly collected from the palm oil mill effluent (POME) [4]. SPO has bad odour, low quality, high viscosity, dark brown or black in colour but has the potential to become biodiesel feedstock as it comprises significant features. At times, SPO is used as the main material for the production of low-quality soap while most of them were treated and disposed as waste. High free fatty acid (FFA) present in the oil is the primal element that hinders the application of SPO to directly produce biodiesel as it resulted in undesired soap formation [5]. Therefore, pre-treatment of SPO is necessary prior to biodiesel production as the allowable FFA value is 3% or below [6].

The method that is capable to reduce the FFA and directly act as the pre-treatment process is glycerolysis. It is basically the addition of glycerol with the aid of catalyst at high temperature. The rationale of glycerolysis is the abundant FFA will react with glycerol to form glycerides; monoglyceride, diglyceride or/and triglyceride. Triglyceride is an important component in transesterification to produce biodiesel. On top of that, glycerol is the main by-product acquired upon production of biodiesel

through the common transesterification method. It is an advantage to promote glycerol reusability and indirectly reduce the cost. Furthermore, glycerolysis method can be enhanced by optimizing the operational conditions such as temperature, catalyst loading, and oil to glycerol mol ratio. The parameters can be modified and improvised to increase its efficiency to obtain the optimum result.

In this research particularly, SPO was collected from POME located in Kemaman, Terengganu before being tested for its characteristics including FFA value, moisture content, saponification value, functional groups, fatty acid composition and chemical composition. This step was done to briefly observe its capability to produce biodiesel. Then, glycerolysis was performed with the aid of zinc oxide (ZnO) as catalyst. Different parameters were applied to assess its efficacy to reduce the FFA accordingly. The treated SPO with low FFA value (<3%) were then applied to produce biodiesel. Transesterification was then performed to produce biodiesel by using ethanol as reactant and potassium hydroxide (KOH) as catalyst. The produced biodiesel was then analyzed to verify the presence of fatty acid ethyl ester (FAEE) to authenticate the successful of biodiesel production. Figure 1.1 portrayed the brief flow of the production of biodiesel from SPO with the addition of pre-treatment reaction by glycerolysis.

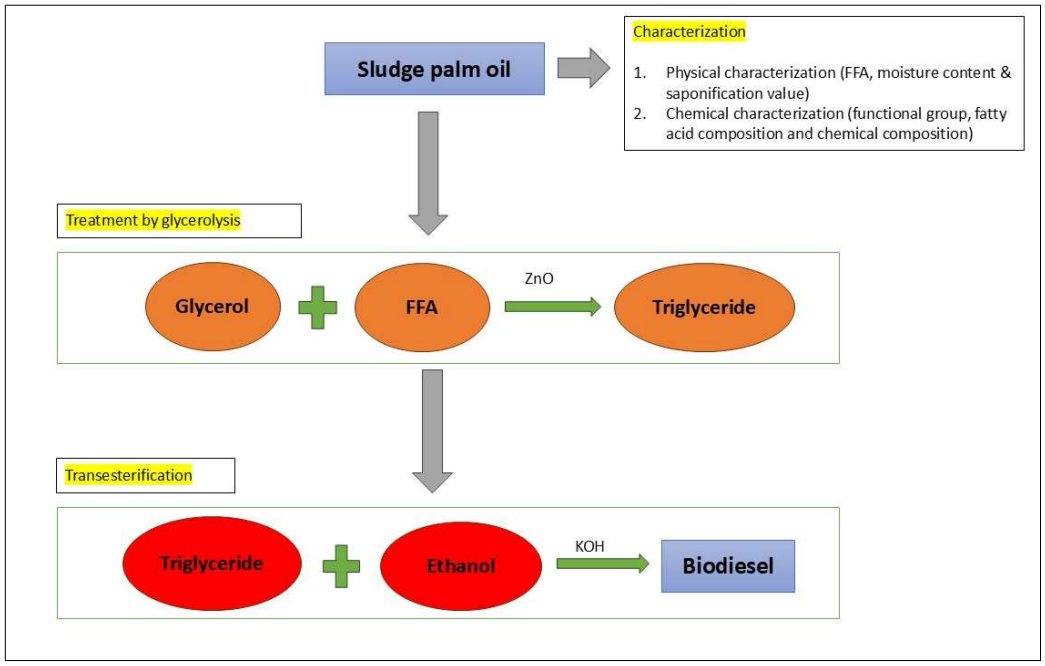


Figure 1.1 Brief Flow From SPO To Biodiesel Production

1.2 Problem Statement

The application of biodiesel to fully replace the conventional petroleum diesel is limited due to the huge price difference as well as unethical issue. About 80% of the total cost of biodiesel is contributed by the cost of the feedstock that infers the price issues on its raw materials. The common feedstocks which are vegetable oils such as palm oil, sunflower oil and canola oil rise some issues that includes high cost due to the demand competition with food industry. Ethical issues emerged because the edible vegetable oils raising food vs fuel crisis and alarming food securities [7]. Therefore, it is crucial to explore other feedstocks that are not edible and low in cost but capable to transform into biodiesel.

SPO is a feasible candidate due to its promising features including renewable and high availability. The characteristics of SPO are similar to the common feedstock of biodiesel. However, the presence of high FFA in SPO is a major drawback that caused significant consequences upon biodiesel production. The issues associated with high FFA in oil feedstocks are: (1) formation of undesired soap, (2) reacts as emulsion and (3) minimize the yield of produced biodiesel. The content of FFA of typical SPO can go up to 80% which is believed as high value that is more complex and difficult to reduce [5]. Hence, theoretically, pre-treatment of SPO is required to lower down the value of FFA first before producing biodiesel.

The typical method used to reduce the FFA in waste oils are acid-catalyzed esterification where methanol is employed with the aid of strong acid as catalyst. Although this method is qualified to eliminate the FFA in oils, some downsides of this method are often observed which are: (1) high ratio value of methanol needed, (2) high cost of methanol, (3) low boiling point of methanol that may vaporize upon heating, (4) corrosive acid catalyst and (5) the possibility for the acid catalyst to neutralize the alkali catalyst in transesterification that resulted in less reaction [8]. Therefore, in this study, glycerolysis method is selected as a suitable technique to tackle these issues. This method does not require high ratio value of reactants, provides high efficiency, promotes reusability of waste by-products and avoids corrosive equipment [9]. The efficacy of the method is highly influenced by many variables that should be studied and investigated further [10].

1.3 Research Objectives

The aim for this study is to achieve the stated research objectives as below:

a) To determine the physical and chemical characteristics of Sludge Palm Oil (SPO)

b) To investigate the effect of temperature, SPO to glycerol mol ratio and catalyst loading to the reduction of FFA in SPO using glycerolysis

c) To investigate the ability of treated SPO with lowest FFA content as biodiesel feedstock

1.4 Research Question

Questions that built up prior to this research are as below:

i) What are the characteristics of the Sludge Palm Oil (SPO) to make it qualified to be biodiesel feedstock?

ii) Is SPO feasible to be biodiesel feedstock?

iii) What is the most efficient and practical way to reduce the FFA in SPO?

iv) What is the lowest value of FFA can be achieved by SPO using glycerolysis?

v) How to promote the reduction of FFA by glycerolysis?

vi) What are the significant parameters in obtaining optimum results through glycerolysis?

vii) Is it feasible to produce biodiesel from the treated SPO through glycerolysis?

1.5 Significance of Study

The main highlight of this study is the concept of waste-to-wealth that are significantly developed. Malaysia is one of the biggest producers and suppliers of palm

oil base products, exporting to various countries. It is recorded that Malaysia imparts around 25% of worldwide palm oil production with up to 30% of global exportation [11]. Therefore, it is apparent that amount of waste from the palm oil mill is inexhaustible. Considering that SPO is collected from the POME, this denotes the large and abundance amount of SPO, especially in Malaysia. Furthermore, only small volume of SPO has been used for production of soap and animal feed, while the remaining is treated as waste. After being treated in the treatment plant, they usually been disposed in drainage, riverbanks or lands in the specific standards required by Department of Environment (DOE). However, there are slight likelihood that these wastes were not treated properly according to the standards by irresponsible owners that resulting in polluting the environment when they were being discharged. In addition, this feedstock is cheap that can be taken as advantage to be transformed into source of energy. Therefore, this study is profound in applying this abundant waste as biodiesel feedstock to convert into biodiesel that is significant to help in reducing the pollution to the environment.

On top of that, instead of using other methods such as acid catalyst esterification and enzymatic esterification, glycerolysis method is used as a pre-treatment process to reduce the FFA in SPO. The significance of this method is the fact that the FFA been reduced not by removing or extracting them out from the oil, but by converting the FFA into glycerides with glycerol as the reactant. These produced glycerides will be the main constituent for biodiesel production. Another notable reason is that glycerol can be obtained from the by-product of biodiesel production, that can be recycled to treat the SPO, which can lower the waste production as well as operational cost.

Furthermore, the application of ZnO as the catalyst as an aid to accelerate the glycerolysis reaction is also vital. The advantage of employing metal oxide as catalyst has proven by other studies to be effective due to its heterogeneous nature and the ability to promote the synthesis of triglyceride. Though there are only few studies on applying specific ZnO in glycerolysis, ZnO is regarded to perform efficiently because of its unique feature including high catalytic performance, high FFA tolerance and environmentally friendly [12, 13].

Generally, this study promotes the effort of utilization of biodiesel as an alternative to replace petroleum fuel globally and permanently. This study is able to assist in solving the issue of the expensive cost of biodiesel production and the low availability of raw material by using SPO as the feedstock. The sustainable development

goal (SDG) especially SDG 7 that is affordable and clean energy can be achieved when the production and implementation of biodiesel application is enhanced with greater convenience and lesser cost.

On top of that, it is important to highlight the research gap involved to significantly justify the need for this study. According to Table 1.1, it is shown that there were various studies have been performed by other researches previously that regarding the issues highlighted in this study. However, it reveals that there was not yet findings on the reduction of FFA using glycerolysis, specifically in SPO. Moreover, research on employing metal oxides like ZnO to reduce FFA by glycerolysis has not yet accomplished by other researchers. Hence, based on the gap analysis, it is essential to emphasize the necessity of for further investigation of this study.

Table 1.1
Gap Analysis For This Study

Study	Remarks	References
Characterization of SPO	There were numbers of researches studied on the physiochemical of SPO.	[14]
Utilization of SPO to produce biodiesel	Few studies on application of SPO to biodiesel. The latest one was on 2024, using acid catalyzed esterification method.	[15, 16]
Reduction of FFA in waste oils using other method than glycerolysis	The common method used was acid catalyzed esterification, using methanol as the reactant to reduce FFA in waste oils including used cooking oil.	[17, 18]
Reduction of FFA in oils using glycerolysis	Glycerolysis method has caught attention to reduce FFA significantly, in various oils including crude palm oil.	[9, 10, 19]
Reduction of FFA in SPO using glycerolysis	This study has not been done yet.	-
Utilization of metal oxide in glycerolysis	This study has been done, but not specifically to reduce FFA in oil.	[20]

1.6 Thesis Scope

This study mainly focuses on utilizing waste, which is SPO that is obtained from Kemaman Palm Oil Mill in Terengganu. The SPO is characterized into two classes which are physical and chemical characteristics by several tests. The tests consist of FFA value, moisture content, and saponification value for physical characteristics while

fatty acid composition (by using Gas Chromatography- Flame-ionization detection (GC-FID)), functional group (by using Fourier-transform infrared spectroscopy (FTIR)) and chemical composition (by using Gas Chromatography – Mass Spectrometry (GC-MS)) for chemical characteristics. These characterizations were then compared with Crude Palm Oil (CPO) to analyze the feasibility of SPO to produce biodiesel. The characterization is needed to assess that SPO is qualified as biodiesel feedstock but only requires some treatment. The SPO is treated by reducing the FFA content through glycerolysis. Pure glycerol is used as the reactant with ZnO (powder form) as catalyst to assist the reaction. The reaction time was limited to 3 hours to monitor the reduction of FFA.

The limitation of this study is primarily based on the three different parameters that are tested to obtain the optimum result. The parameters include temperature, catalyst loading and SPO to glycerol mol ratio. The temperatures are varied at 170°C, 190°C and 220°C. The catalyst loading will be tested at 0.25%, 0.50% and 1.0% to obtain the sufficient amount of catalyst that is required to reduce the FFA within standard while preventing excessive loading. In order to promote triglycerides and reduce the FFA effectively SPO to glycerol mol ratio is varied at 1:1, 1:1.5, and 1:2.

Furthermore, in this study, the reduced FFA SPO is used to perform transesterification method to produce biodiesel by using ethanol. The produced biodiesel is then analyzed by FTIR and GC-MS to verify the accomplishment of the production. The scope of this study is to authenticate the feasibility of SPO to transform into biodiesel, by carrying out glycerolysis prior to transesterification. The formation of fatty acid ethyl ester in the product from the analysis confirms the hypothesis.

1.7 Thesis Outline

This thesis specifically intends to guide readers on the investigation of the implementation of glycerolysis to reduce high FFA in SPO as an effort to employ the SPO to become biodiesel feedstock.

Chapter One is a brief introduction the research to get a clear picture on the study. It comprises of its research objectives and problem statements to clearly understand the significance of the study.

Chapter Two is “Literature Review”, it sums up the related previous studies by researchers that related and interconnected with the study. A brief review on biodiesel

is presented to grasp the importance on the production of biodiesel. After that, SPO is introduced to view its features, potential applications, benefits etc.

Chapter Three or “Research Methodology” basically present the step-by-step method executed for the overall research. Mainly the methods are divided into three major phase that related with research objectives. There are: (1) Characterization of SPO, (2) Glycerolysis of SPO with different parameters and (3) Production and analysis of biodiesel. The detailed procedures are explained in this section.

Chapter Four; “Results and Discussion” is one of the important sections of this research which demonstrate the results obtained from the implemented methods. Graphs and figures are presented to exhibit the analysis from the study. The characterization of SPO is discussed and compared to previous study. Graphs for the glycerolysis method for each parameter are presented and then been evaluated and discussed. The analysis for production of biodiesel is also investigated and evaluated to review the success of the study.

Chapter Five concludes the whole study and deduced the overall research. Conclusion based on the results and discussion are proposed to denote the achievement of the study which is SPO has the potential to become biodiesel feedstock. Future prospects and recommendations on glycerolysis are also discussed in this section to suggest the improvement that can be made for better study in the future.

CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

Energy security is one of the most predominant elements in this emerging global development that needs to take attention and action promptly. The forecast of global energy consumption by International Energy Agency is projected to reach up to 225 quadrillion Btu by the year of 2040. This depicts a drastic increment of approximate 55% when compared to the year of 1990 [21]. The primary source of energy that are widely applied globally for various purposes is from fossil fuel. High dependency towards this source has raised tremendous concerns due to limited resources and reserves declination [22]. Petroleum diesel, a common example of fossil fuel are used extensively in transportation industry as engine oil for buses, trucks, boats as well as in generators to generate electricity [23]. Immense application of petroleum diesel has caused detrimental effects towards the environment and humans' health. The main source of greenhouse gas (GHG) emission that resulting in global climate change is from the extensive application of petroleum diesel. [24]. The intractable release from fossil fuel consumptions of poisonous components such as sulphur oxides, nitrogen oxides and volatile chemicals to the atmosphere have resulting to bad impacts towards humans' health [25]

Due to the energy insecurity incorporated with the atrocious effects to the environment and human health, the world emerges to acquire potential source as everlasting solution. For those inevitable reasons, a comprehensive strategy should be developed to stabilize and balance the energy demand and consumption with the resource availability. On top of that, exploring the replacement diligently would be a response and effort of the universal call towards Sustainable Development Goals (SDG) especially SDG 7 and SDG 13 which are affordable and clean energy and climate action. Thus, it is crucial to search for alternative energy source that comprehend similar features but has abundance supply, sustainable and cleaner to the environment.

2.2 Biodiesel

Over the years, the exploration of biodiesel has evolved rapidly due to its attractive attributes. Biodiesel is one of the most promising options to replace fossil fuel for a long-term solution as it has significant qualities that are renewable, sustainable with high availability feedstocks, environmentally friendly, biodegradable, high technical feasibility and easy to implement. Application of biodiesel has predominantly contributed to the reduction of carbon dioxide emission at least by 50% [26, 27]. Furthermore, comparing to the conventional fossil based diesel, it has better autoignition capability with excellent lubricity and high cetane number [28]. The comparison of properties for biodiesel and conventional petroleum diesel are tabulated in Table 2.1. Upon comparing biodiesel with the conventional petroleum diesel, the presence of acid number and higher number of sulphur content and viscosity in biodiesel is presumably due to the selection of biodiesel feedstock. Conveniently, biodiesel can be used either directly or blend with conventional diesel fuel without outstanding moderation. It is also compatible with diesel engine which makes it instantly accessible [29].

Table 2.1
Properties Of Biodiesel (BD) And Conventional Petroleum Diesel (PD) [30-32].

Properties	Unit	BD	PD
Sulphur content	ppm	160	80
Kinematic viscosity at 20°C	10^{-6} m^2/s	6.9	4.4
Cetane number	-	55	51
Flashpoint	°C	130	55
Aromatics	% mass	-	11
Acid number	mg KOH/g	3.52	-
Density	kg/m^3	875	845
Cloud point	°C	-1	-
Viscosity	mPa·s	4.7	2.8
Water content	% w/w	<0.1	<0.1
Specific gravity	mg/mL	0.89	0.85

Fatty acid alkyl ester that is biodiesel is mainly produced from lipids that are originated from edible or non-edible oils, animal fats, and algae. Global biodiesel production is projected to exceed 41.4 billion litres by 2025 that is 33% increment from the year 2015 [33]. Malaysian Palm Oil Association (MPOB) has forecasted slight

increase of production of biodiesel this year that is about 19.5 million tonnes of crude palm oil, from 19.34 million tonnes in 2024. This projection is high likely driven by the surge of demand of biodiesel, especially from Indonesia [34]. Environmental consciousness, government regulations promoting renewable energy, and advancements in technology are the main antecedents that contribute to the rapid inclination of biodiesel production and application globally. The positive increment of the biodiesel production forecast demonstrates the substantial demand for biodiesel that leads to the urge of global transition from non-renewable to a sustainable major energy source in various sectors [2, 35].

Although it is remarked that the production and application of biodiesel is arising, it is still discernible that there is a tough competition with the conventional diesel in various application. This scenario is shown by the declination of large number of parties to participate in the full transitions to biodiesel as major source of energy. The reasons for this are primarily due to: (1) expensive, around 3 times more costly than conventional petroleum diesel (2) inadequate and unavailability of resources and (3) insufficient technology [36, 37].

2.2.1 Transesterification Method

The production of biodiesel can be executed in various procedures including transesterification, microemulsion, pyrolysis, dilution, enzymatic transesterification, and supercritical fluid technology. However, transesterification method is the most common and potent strategy to produce biodiesel as it non-complex, convenient, reputable and cost-effective [38]. Other contributing factors for the vast application of transesterification method upon producing biodiesel is the high yield of biodiesel with only low temperature, pressure and reaction time required. These would be a plus point for energy conversation and cost minimization [39].

As portrayed in Figure 2.1, biodiesel production by transesterification method is carried out by reacting triglyceride with short-chain alcohol (eg. ethanol) with the aid of appropriate catalyst (e.g. KOH) to produce fatty acid alkyl ester which is the biodiesel and glycerol as by-product. Triglyceride is a type of fat and esters of three fatty acid and one glycerol that is commonly present in vegetable oil and animal fats. Basically, the rationale of this reaction is the transforming of one ester into another ester by an exchange or translocate of the OR group [40]. Substantial excess amount of alcohol is

necessary in order to complete the reaction and to hinder reverse reaction as the reaction is reversible. The alcohols that are commonly employed as the reactant for this reaction are ethanol and methanol since they conspired of shortest chain length that contributing to a high reactivity.

Methanol is the most utilized alcohol for this reaction reported in many researches as it only needed simpler technology and high likely to achieve higher reaction speed at lower cost [14, 41, 42]. However, comparing methanol to ethanol, ethanol offers numbers of advantages including higher solubility, higher sustainability, safer and cleaner. First, ethanol provides higher solubility in oil that helps in enhancing the reaction by improving the miscibility between the alcohol and the lipid phase. The high solubility facilitates better mass transfer and more efficient contact between reactants that ultimately enhancing the reaction rates and conversion efficiency. On top of that, it is acknowledged that ethanol can be acquired from renewable source that promotes sustainability. Ethanol can be produced from several biomass sources such as sugarcane, corn, or lignocellulosic feedstocks that implying the significance of circular and sustainable energy system. In contrast, methanol is commonly derived from fossil fuels, which contributes to greenhouse gas emissions that impacting to pollution. This subsequently reduces the overall sustainability of the process. Third, ethanol is considered safer and cleaner than methanol because it is less toxic to humans and the environment. Methanol is highly poisonous and poses significant health risks through ingestion or inhalation, whereas ethanol is comparatively benign and is widely used in food, pharmaceuticals, and consumer products. Hence, the use of ethanol in this study not only highlight the process performance but also aligns better with environmental safety and sustainability goals [43]. Furthermore, there are only few studies on applying ethanol for transesterification of treated waste oils despite the mentioned advantages. Therefore, in this study particularly, ethanol is applied to further study the transesterification reaction of the treated SPO to produce biodiesel.

Basically, transesterification reaction transpires in three orderly steps which are: (1) conversions of triglyceride to diglyceride upon reacting with ethanol, (2) further reaction with ethanol to convert diglycerides to monoglycerides and (3) monoglycerides reacting with ethanol as conversion to fatty acid ethyl esters and glycerol [44]. Assuming single-step reaction is applied, the intermediate reactions of diglyceride and monoglyceride can be disregarded. Therefore, it is stoichiometrically valid to affirm that 3 mol of ethanol and 1 mol of triglyceride is vital for this reaction to occur [45].

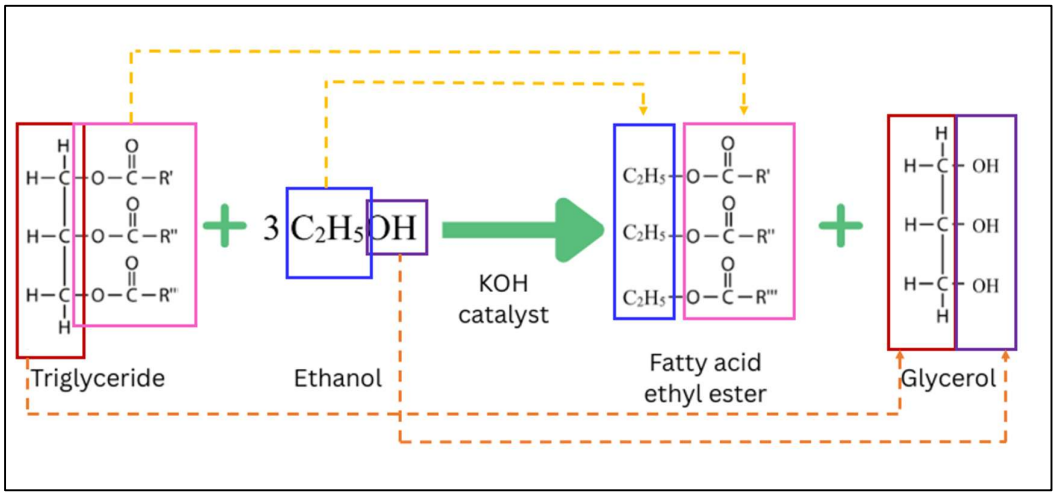


Figure 2.1 Transesterification Method To Produce Biodiesel.

Glycerol as by product is also a bonus point in this reaction as it can be utilized for other significant products [46]. Monteiro et al. studied that crude glycerol obtained from the biodiesel production are typically applied for chemical products, polymer compounds, and production of biofuel [47]. It is favourable for waste alleviation and also economically viable. On top of that, glycerol collected from the by-product of biodiesel production can be utilized for glycerolysis process. Study by Suriani et. al. reported the ability of crude glycerol from transesterification process to reduce FFA in CPO by glyecerolysis method [48].

In transesterification, catalyst is a vital element that assist in promoting the reaction rate and increasing the alcohol solubility by reducing the activation energy. The selection of catalyst is influenced by the designated feedstock of biodiesel. Types of catalysts that are usually applied for transesterification are base-catalyst, acid-catalyst, heterogenous catalyst and enzymatic catalyst. The most common used catalyst in order to carry out transesterification efficiently is base-catalyst. There are plenty of significant ground to this option comparing to others which include fast reaction, high yield, low cost, non-corrosiveness effect and low toxicity [49].

The typical alkali used for base catalyst are Potassium Hydroxide (KOH) and Sodium Hydroxide (NaOH). These alkalis are low in cost and effectively assisting transesterification at higher reaction and faster time. Biodiesel can be produced productively with the yield of 98% with moderate condition of temperature and pressure at short time [50]. However, the productivity of these alkalis in aiding transesterification is influenced by the presence of free fatty acid (FFA) and water within the reaction. These two components may disrupt the reaction and consequently, affecting the

production of biodiesel. Mainly, only 3% or lower of FFA with minimum amount of water is advised in the feedstock to run transesterification with base catalyst [51]. High amount of FFA resulting in soap production when react with alkali and indirectly reduce the yield of biodiesel. This phenomenon is shown as in Figure 2.2 that displayed the possible reaction of soap formation. The excess amount of free fatty acid tends to synthesize with the alkali catalyst like NaOH to produce undesired soap and water. On the other hand, excess water tends to hydrolyse triglyceride and produces more undesirable FFA [52]. Hence, it is crucial to assure there is minimum amount of FFA and water in the feedstock in order to produce biodiesel efficiently.

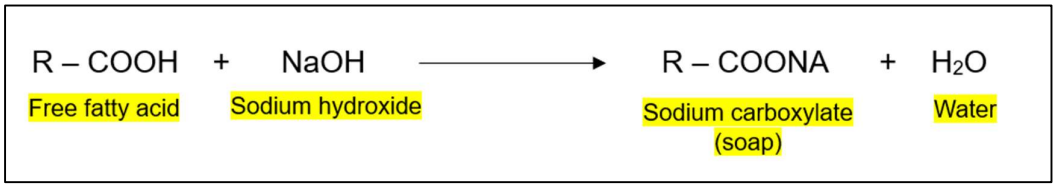


Figure 2.2 Reaction Of FFA With NaOH That Produces Soap [52].

2.2.2 Biodiesel Feedstock

One of the positive aspects in biodiesel is the variety versions of the feedstocks. Considering the main element to produce biodiesel is triglyceride, researchers have worked for years to discover the possible sources that are capable to form biodiesel efficiently. Mainly, the feedstocks of biodiesel are divided into several categories, each possess its own benefits and disadvantages, depending to its usage and condition. The selection of feedstocks is commonly depending on some aspects as follow: (1) geography and location, (2) resources availability, and (3) economic viability. As shown in Table 2.2, the generations of feedstocks for biodiesel production over the years are demonstrated.

First generation of biodiesel feedstock that is edible oils are the most typical, dominating the other feedstocks in the application of biodiesel. However, it has numbers of issues that are perturbing and urges for other feedstocks discovery. Hence, the exploration of second generation which are non-edible oils originated from plants perceives as promising plan but the toxicity concerns along with land use competition conveyed limitations of promoting this feedstock. Therefore, waste based containing fats sourcing from animals, cooking oils and other oils attracting researchers to venture

in experimenting the aptitudes to produce biodiesel. It has recorded that this generation has efficiently taper down the production cost and navigate the land use issues but require pre-treatment process. Both fourth and fifth generations are still in early stage with limited technology and study but offers great alternative potential [35].

Table 2.2
Biodiesel Feedstock.

Generations	Feedstock	Examples	Advantages	Disadvantages
First [53-55].	Edible oils	Soybean oil, corn oil, palm oil	Simple conversion technology	Fuel vs food crisis and expensive feedstock due to the high competition with food industry
Second [53-55].	Non-edible oils	Jatropha oil, jajoba oil	High oil content and high adaptability	The toxicity of seed cake and high cost
Third [53, 54].	Waste based	Waste cooking oil, animal fats	Valorization of waste streams	Required pre-treatments
Fourth [53, 54].	Algal biomass	Microalgae, macroalgae	Grows easily and do not need land	High cost and inadequate biomass production
Fifth [53, 54].	Genetically modified organisms	Cyanobacteria	High biomass production	Limited technology and study with high capital cost required

Among all five generations, edible oils that commonly sourced from vegetable oils like palm oil and soybean oil are the most prevalent feedstocks that are regularly employed to produce biodiesel. Essentially, around 70% of global production of biodiesel is originated from the first generation which accommodate the majority of biodiesel feedstock [56]. The rationale of applying these oils is due to its copious content of triglyceride with minimal impurities. As shown in Figure 2.3, palm oil, rapeseed oil and soybean oil produce biodiesel by 32%, 14% and 23% respectively. Palm oil has been the predominance vegetable oil that are selected consistently as biodiesel feedstock especially in Indonesia, Malaysia and Thailand. The ground for this phenomenon is highly contributed to the abundance resource of palm oil in the mentioned countries which then significantly promote the application of biodiesel. Previous study achieved 94% yield of biodiesel when using CPO as the feedstock [57]. On the other hand, United States is one of the largest producers of soybean oil due to its excess supply and established cultivation practices. Therefore, in the United States as well as Brazil, soybean oil is preferable as biodiesel feedstock. In Germany,

approximately 60 to 70% of biodiesel distribution feedstock comprises of rapeseed oil because of its profusion, contributing by its location and cultivation ability factors [58].

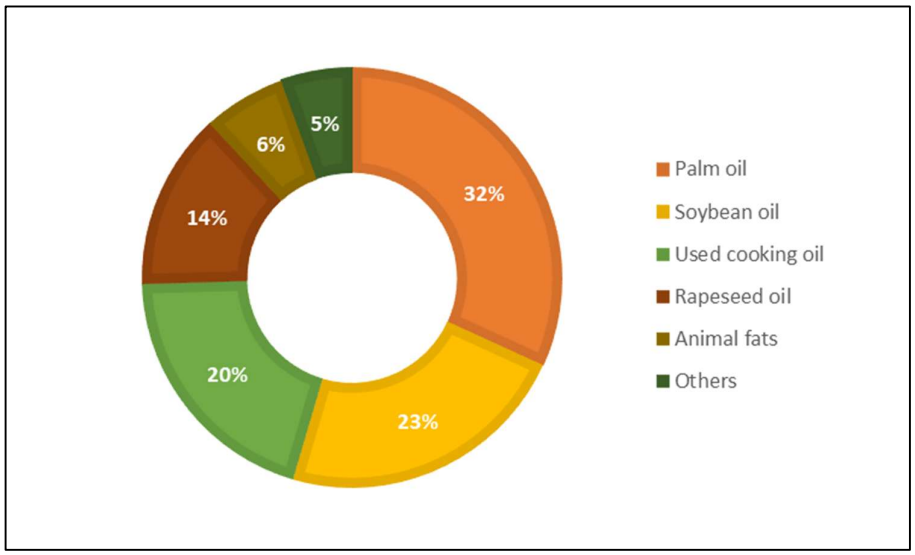


Figure 2.3 Global Biodiesel Feedstock [59].

However, the application of vegetable oils has escalated numerous relevant predicaments that are alarming to various aspects. The main problem associated with the widespread of biodiesel derivation by these vegetable oils is the expenditure. This issue can be observed in Figure 2.4 where the cost distribution to produce biodiesel is presented. A percentage of 75% represents the feedstock which conquer large fraction of the total expenses of biodiesel production. This phenomenon implies that the reason for the huge gap of the cost comparison between biodiesel and petroleum diesel is majorly contributed by this matter. It also indicates that if the challenge of the vast expense of the oil feedstock can be resolved, the cost of the energy, direct labour, chemical feedstock, and general overhead of biodiesel production are undeniably low. The apparent reason of the elevated cost is because of the presence of competition with the food industry. Since these vegetable oils are edible and are generally utilized to produce food to consumers, the demand of application to generate fuel from this source leads to the increment of the basis price [32].

On top of that, there is an established debate regarding the unethical issue in exploiting food source for energy purposes. Employing edible oils for fuel application may become a probable threat to the food security especially for countries that are more affected by the crisis. The debate of food vs fuel has alarmed the society and researchers as unethical because of the exploitation of food resource, land use change, and resource intensive. Extensive production of vegetable oils for energy intention requires immense

inputs from land, water, fertilizers, and energy that contributing to the environmental effects [60].

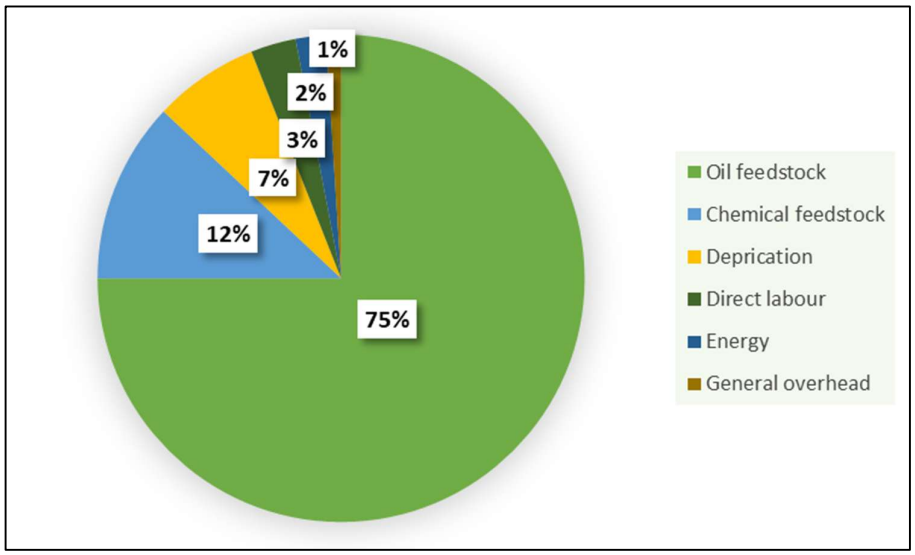


Figure 2.4 Biodiesel Production Cost Distribution [61].

Therefore, a significant transition is required promptly from applying vegetable oils as the main biodiesel feedstock throughout the world. The evident limitations have unfolded the inevitable drive to shift to other source of feedstocks in order to hinder the expected detrimental event in the future. The application of vegetable oils should be discontinued or scaled down as mitigation to the respected issues. Other generation of biodiesel feedstock should be studied, explored, and invested rigorously to enhance and promote the application of the source as a dominant feedstock to produce biodiesel.

There are few attributes that can contribute significantly as a feasible and excellent feedstock to produce biodiesel. The ultimate vital elements include high sustainability, cost-effective and possessed physiochemical properties that adhere to the specific standard of biodiesel feedstock [10]. While selecting the right raw material to produce biodiesel, the component should not be in the food chain competition and required minimum amount of land and resources to ensure the sustainability. On top of that, essential characteristics including low FFA values, iodine values and moisture content are important to take into consideration to ensure the efficacy of synthesis of biodiesel [54]. The physiochemical characteristics of good candidate of biodiesel feedstock are summarized and tabulated in Table 2.3. Therefore, it is important to select a high reliable and feasible feedstock to produce a high quality of biodiesel.

Table 2.3
Physiochemical Characteristics Of Biodiesel Feedstock.

Characteristics	Range/limit	Reference
FFA (%)	< 3	[7, 37, 62]
Acid value (mg/g)	< 2	[7, 62]
Saponification value (mg/g)	180 – 210	[3, 54]
Moisture content (%)	< 0.06	[3, 54]
Iodine value (I_2 g/g)	120 / 100	[63]

2.3 Palm Oil

The production of palm oil is one of the largest and important vegetable oils produced across the world with the quantity of 79.1 million tonnes in the year of 2024 [64]. Asia countries including Indonesia, Malaysia and Thailand contribute to the majority production with an approximate of 87% of total production [65]. In Malaysia alone, Malaysian Oil Palm Industry has recorded up to 18.4 million tonnes of crude palm oil (CPO) processed sourced from 87.9 million tonnes of fresh fruit bunch (FFB). Furthermore, there are a substantial amount of 450 palm oil mills in Malaysia that encompass up to 5.7 million hectares planted area that indicates its prominent virtue [66]. It is also stated that these mills operate with distinct capacity ranging from 20 tonnes per hour to 120 tonnes per hour, depending on the magnitude of the plantations. It is established that palm oil resources in Malaysia particularly is large and abundant.

Essentially, from the FFB collected from the plantation, there are two indigenous products that are the core output for the formation of palm oil. Crude palm oil (CPO) is the end product processed from the outer part which is the pulp of the fruit bunch while palm kernel oil (PKO) is extracted from the soft part of the seed. From these native oils, there are plenty of other oils that are formed subsequently from sequence of process such as refine, bleach, and deodorize oils. These variations of oils have their respective vital applications in various industries such as fuel, food application, and cosmetics.

Ultimately, CPO is the primary product of palm oil that offer extensive application and profit centre in the palm oil industry. The primary applications of CPO are cooking oil, food ingredients, and food additives. On top of that, lubricants in industrial sector are conventionally employ CPO as their main raw materials and as mentioned in previous section, CPO is widely used as biodiesel feedstock as fuel

application. There are abundant studies reported the production of biodiesel from CPO [67]. CPO mainly comprise an approximate of 20% of FFB after going through series of process including sterilization, stripping, digestion and pressing. Typically, 90% to 95% compositions within CPO consists of triglyceride, diglyceride, monoglyceride and free fatty acids which are the major elements. The predominant fatty acid presence in CPO is palmitic acid. The remainder of 5% to 10% are generally identified as the minor elements which comprises of carotenoids, tocopherols, sterols, phosphatides, and aliphatic alcohols [68]. CPO is generally appeared in reddish-orange colour and semi-solid phase in room temperature with nutty odour. The properties of CPO as in Malaysian crude pam oil standard by are presented in Table 2.4.

Usually, the operation of extracting CPO until the end-product is acquired may most likely resulting in a low free fatty acid CPO with capacity of free fatty acid less than 5%. However, some influential factors like storage condition, climate change, and humidity can affect this circumstance and ensuing to a higher composition of free fatty acid. It was reported diligently that CPO with higher than 5% of FFA composition is not safe for human consumption thus discarding its application in food industry [69]. In addition, CPO with excess amount of FFA is provenly sabotaging the yield of fuel which indicate its deficiency in quality. Therefore, it is crucial to ensure the FFA level within the CPO composition as indication of the quality of the oil.

Table 2.4
Properties Of Malaysian Standard Crude Palm Oil [70].

Properties	CPO_{MS}
FFA (%)	< 5
Acid value (mg/g)	< 5
Saponification value (mg/g)	194-205
Moisture content (%)	< 0.25
Iodine value (mg/g)	50.4 – 53.7

CPO_{MS}: Malaysian standard crude palm oil

2.4 Sludge Palm Oil

As mentioned in previous section, palm oil conquers the majority of the edible oils that are utilized as the main raw materials to produce biodiesel as it possesses tremendous qualities. However, owing to the substantial issues mentioned in applying edible oils for fuel purposes have brought intend transition to shift into other potential

feedstocks. It is discernible that the next suitable feedstocks that should be brought into attention are non-edible, high sustainability, renewable, environmentally friendly, cost-effective and has high efficiency. Since palm oil is appraised as one of the best and prime feedstocks, selecting other raw materials to produce biodiesel that derived from this oil would be appropriate, reasonable, and effective.

Typically, waste from palm oil production in every palm oil mill will be treated as palm oil milling effluent (POME) in the treatment plant before being discharged to the assigned water course or land. POME is mainly comprised of wastewater sludge with approximate content of 95% of water, 4-5% of organic solids, 0.5-1.0% of unrecovered oil with contamination of grease, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) [71]. Due to the drastic demand and supply of palm oil, bulk quantities of POME are also produced simultaneously. Identified authorities are responsible in governing the disposable management of POME, such as Department of Environment (DOE) Malaysia with respected regulations and acts. However, palm oil industries have been condemned due to some irresponsible parties that resulting in lack of management on POME. Large amount of POME has contributed to this scarcity to discharge POME safely. This event then leads to negative impacts to the environment including soil pollution and exposure of harmful gases such as methane gas that contributing to greenhouse gas emission. Hence, rather than treat and discharge, it is highly recommended to transform the abundance POME into sorts of energy, as mitigation efforts to tackle the problems [5].

SPO, that is a certain fraction of POME is viewed as a potential candidate to replace palm oil as primary feedstock of biodiesel. Mainly, SPO is collected from the top oil layer of POME that has passed through equalization phase. According to Figure 2.5, it is approximated that 67% of processed fresh fruit bunch (FFB) collected from the palm oil plantation is commonly treated as POME while only 20% will be produced as crude palm oil (CPO) to be commercialized. Based on an analysis, SPO comprises of approximate 1.5wt% from the CPO which totalled a round of 33 million tonnes in Malaysia alone upon observing the 2022 statistics [72]. However, in industrial perspective, in order to design treatment plant for the respective mill, the quantity of POME is presumed as 1 to 1 ratio with the pre-operational FFB. This situation implies that the quantity of POME is excessive and resulting to a larger scale of SPO.

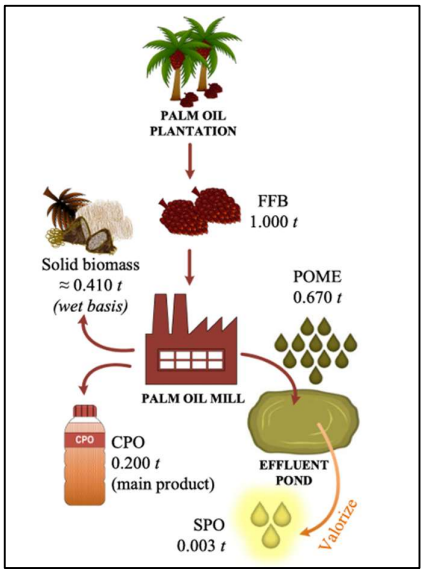


Figure 2.5 Key Inputs And Outputs Of Palm Oil Milling Processes [4].

Essentially, SPO is tolerated as waste with non-edible and low-quality features but possesses the significant attributes of palm oil. SPO is commonly has bad odour with dark brown to black colour. It exists in semi-solid phase in room temperature and its melting point is around 50°C. Considering SPO is discarded from palm oil production, the composition within SPO is mainly free fatty acid, glycerides and other impurities. The further properties of SPO are exhibited as in Table 2.5 [73]. The acid value, free fatty acid content and moisture of SPO are impactfully high that lead to deficiency of oil. These factors have resulted in very cheap SPO. According to the daily Malaysia price of crude palm oil published by MPOB, the latest price in the market of CPO can go up to RM 4,850/tonne. While SPO is usually quoted at 50% or lower of this price, it can be exploited to replace CPO for significant applications [14]. In some frame of reference, SPO is collected in a minimal quantity for low-cost soap or animal feed production. However, there is an abundance of SPO that commonly being treated as waste and to be disposed and discharged to the environment. This circumstance occurs is contributed by the factor of the inability of SPO to be reused as fuel or energy to the mill. Additional concerning factors including the dysfunctional waste management and irresponsible parties that affective the environment due to the excess amount of SPO. Discharging SPO to the land or water course not within the standard implemented by the government by unaccountable entities have resulting in soil pollution and contaminating the aquatic environment [5].

Table 2.5
Properties of SPO.

Parameters	Unit	Range	Reference
Free Fatty Acid, FFA	%	23 – 93	[14, 74]
Moisture content	%	1.4 – 10.5	[4, 14]
Iodine value,	IV	52.9	[74]
Impurities	%	0.007	[74]
Saponification value	mg KOH/ g oil	206.25	[74]
Unsaponification matter	%	2.37	[74]
Acid value	mg KOH/ mg	50.8	[74]

In the recent past, there are evident interests in SPO to be exploited for other applications. The attentiveness to SPO is increasing in the production of rhamnolipids, a class of glycolipids that are widely used to produce biosurfactants, bioremediation, cosmetics, and others. On top of that, studies regarding the implementation of SPO to produce polyhydroxyalkanoates (PHAs), a naturally occurring biodegradable polymers are also escalating due to its appealing attributes. Both compelling applications are due to the cognizance of SPO as carbon source to the existence microbes. The abundance of SPO incorporating with its remarkable features have captured interests in researchers to venture in experimenting its potential ability to produce value-added products or offers other beneficial outputs [75].

Ultimately, SPO is an ideal prospect as substitute to palm oil for biodiesel production. Owing to its identical characteristics with palm oil and its lipid-rich feature, it is a solid notion to explore the potential of SPO to transform into biodiesel. Furthermore, utilizing SPO as biodiesel feedstock is a bonus point in terms of promoting waste-to-wealth that increases sustainability and as mitigation for environmental impact from palm oil industries. The issues of abundance of SPO that can lead to pollutions due to irresponsible managements can be mitigated by venturing into this study for long-term commercialization. Since palm oil is renewable, reusing its waste is a valuable initiative to advocate for sustainable practices and ecological balances. Additionally, the concept of waste-to-wealth as an initiative to reduce environmental impact while creating valuable products that circulating the economy is applied coherently from this implementation. The abundance of SPO from POME is utilized and commercialized significantly instead of being disposed to the environment [14].

Nonetheless, despite the positive factors, it is impossible to oversee the low-quality aspects of SPO that can contribute to immense impact to the biodiesel production. The most challenging and affecting factor is the inevitable high content of free fatty acid (FFA) in SPO that hinders the conversion to fatty acid methyl ester. Basically, the presence of excessive free fatty acid in SPO promotes soap formation in the process of biodiesel production. This soap formation inhibits the effectiveness of biodiesel by reducing its yield and efficiency. The formation of soap occurs due to the reaction of the surplus FFA with the catalyst in the process of transesterification. This drawback is not affecting enzyme catalyst transesterification since FFA is not the influential factor [15]. However, base catalyst is more common and preferrable catalyst used while performing transesterification in the midst of biodiesel production because it is more cost-effective and high efficiency, comparing to enzyme catalyst. Furthermore, high FFA content correlates to bad quality of the oil.

Therefore, with the aim of applying SPO as biodiesel feedstock, the FFA should be reduced at initial phase prior performing transesterification for biodiesel production. A pre-treatment process is essential to lower down the percentage of free fatty acids within the oil and eventually improve its quality for the preparation to produce biodiesel. This process is necessary to enable the potential of SPO in addition to ensure the effectiveness and increase the yield and efficiency upon the synthesis of biodiesel.

2.5 Free Fatty Acid (FFA)

FFAs are organic compounds of oils and fats that are formed from the breakage of glycerides or oil molecules [76]. The formation of FFA is resulting from hydrolysis of oils and fats due to the exposure of uncertain conditions during storage, heating, processing. The composition of FFA in the oils is influenced by various factors including time, temperature, and moisture content. The level of FFA indicates the quality and performance of the oil. In order to make any oil to become viable for formation of biodiesel, the acceptable level of FFA is at least 3% or lower. On the other hand, FFA in SPO can be varied from as low as 5% to as high as 80%. The degree of SPO depends on the mills' application and the severity of the nature of POME [69].

FFA is strongly undesirable for biodiesel feedstock as they ensuing to unwanted products and situations when reacting with the catalyst in transesterification. As mentioned earlier, the recurrent catalyst used for formation of FAME are base catalyst.

The reaction of excessive FFA with base catalyst tend to promote the formation of soap and water. The formation of soap is an apparent impediment in biodiesel industry as it affects the yield and multiply the viscosity of products. On top of that, the presence of soap enhances the formation of emulsion that complicate the separation of biodiesel with its by-product which is glycerol. Hence, it is evident that oils with high level of FFA cannot be applied directly in transesterification and pre-treatment process is required [23].

There are numbers of attempts studied by researchers to reduce the amount of FFA in oils, especially waste oils. Adsorbent method is one of the examples of technique ventured to reduce FFA in oils. Recent study by Ifa et al. explored the potential of Coconut Coir as bioadsorbent to remove high FFA in CPO and proves its impressive performance [77]. Other adsorbents such as activated cold ash, rise husk and bagasse also are commonly used to reduce FFA in oils including waste cooking oil and used frying oil [78, 79]. However, high complexity process and high production cost are the drawbacks that pull the brakes on these methods to reduce FFA. Physical filtration of FFA is also a notable endeavour in eliminating the FFA. Widiastuti et al. demonstrate the application of polyvinylidene fluoride hollow fibre coated with chitosan to filter out the presence of FFA in CPO [80]. However, the efficiency is limited and require high scale up technology.

Ultimately, the prevalent approach to abate FFA in oils that has been studied by fellow researches throughout the years is esterification method. The rationale of esterification method is by employing alcohol to react with the abundance of free carboxylic acid to form ester and water. Typically, acid catalysed esterification method is implemented to various oils that require FFA moderation prior to further application. Methanol is the primary reactant used as the alcohol reactant to derive with FFA. Sulphuric acid (H_2SO_4) is the common acid used as homogenous catalyst to speed up and increase the rate of esterification reaction. The efficiency of esterification is influenced by the employment of this acid as H_2SO_4 has strong acidity and economical friendly. According to a study, 3wt% of H_2SO_4 at 50°C with 1:6 used cooking oil to methanol ratio has successfully reduced 50% FFA in 60 minutes by performing esterification method [81]. There are numerous studies by scholars to prove the effectiveness of esterification method to reduce the FFA amount in oils [5, 37]. It is also an evident case that the process of lowering down the quantity of FFA is crucial as a

compulsory pre-treatment practice to improve oil quality and boost oil performance for advanced implementation

It is necessary to acknowledge the significant difference between acid-catalyzed esterification and acid-catalyzed transesterification. Acid-catalyzed esterification is the common method to reduce FFA and forming ester while the latter is an effective method of transesterification. Basically, esterification is the reaction of FFA with alcohol to form ester and water while transesterification refers to the reaction of ester and alcohol to form different ester and glycerol.

Acid-catalyzed esterification has been studied for years and the effectiveness of this method has been experimentally proven by the numerous works and the high tendency of selecting this method as the typical pre-treatment process. However, due to its longitudinal study and deep-rooted analysis, apparent drawbacks are often detected. Challenges that are generally developed are related to the extended application of both methanol and sulphuric acid. Apparently, in order to ensure the reduction efficiency, high excess of methanol is required to hinder the reaction to shift to the left. A study reported by Hayyan et al., 6:1 to 14:1 range of volume ratio for methanol with sulphuric acid catalyst are analyzed to acquire the optimum condition that capably reduce FFA in oils. It was found that at 8:1 volume ratio of methanol to oil is essential to effectively lower down FFA content from 23.2% to slightly less than 2% with 93% conversion efficiency [73]. This situation is disfavoured because large volume of methanol is needed that contribute to economic and environmental issue. On top of that, low boiling point of methanol may interrupt the effectiveness of reducing the FFA by vaporizing the reactant upon heating. Furthermore, high acidity of sulphuric acid has facilitated to equipment corrosiveness, environmental concerns due to acid waste generation, yield declination due to enhancement of hydrolysis that may disrupt the process by neutralizing the catalyst [18].

2.6 Esterification By Glycerolysis

The prevailing complications have emerged to shift to other methods or alternatives that can be explored as an attempt to treat oils with high amount of FFA. Esterification method is a symbolic procedure because of the formation of ester that is advantageous as preliminaries to produce biodiesel. However, it is evident that

methanol and sulphuric acid are not the most ideal components that should be used for this method.

Therefore, glycerolysis method is one of a promising alternative to reduce the FFA in waste oils efficiently. Figure 2.6 depicts the chemical reaction involves in the glycerolysis process. It is presented that glycerol acts as the reactant with the existed FFA in the oil with or without the aid of catalyst to produce triglyceride and water. In this study particularly, ZnO is selected as catalyst as a vital tool to assist in the reaction. For better understanding of the reaction, Figure 2.7 displays the reaction occur when glycerolysis reaction is performed. Instead of removing the FFA like the other common methods, glycerol is used to react with the high content of FFA by esterification process which resulting into formation of mono-glycerides (MAG), di-glycerides (DAG) and tri-glycerides (TAG). Generally, the reaction initiate by the activation of the fatty acid, leading by the catalyst. Once the fatty acid has been activated, the hydroxyl group of glycerol that is a nucleophile commenced the nucleophilic attack. As the intermediate formed, the OH group from the fatty acid is protonated, preparing it to leave as water and released a molecule of H_2O. The ester bond is formed between glycerol and fatty acid forming monoglyceride and water. Further reactions occur when excess fatty acid react with monoglyceride to form diglyceride and excess fatty acid react with diglyceride forming triglyceride [82]. Triglyceride is the crucial element that is desired for formation of biodiesel in transesterification reaction. Thus, it is important to highlight that the product synthesized from esterification by glycerolysis is the key factor for production of biodiesel. This context promotes the dominance of this method compared to other conventional methods [83]. Previous report studied the comparison between acid catalyzed esterification and glycerolysis method to the reduction of FFA in waste cooking oil. It was discovered that the final FFA achieved for glycerolysis (19% to 0.4%) was lower than acid catalyzed esterification (19% to 3.2%). The operating condition applied for glycerolysis was at 1.6wt% of KOH catalyst at 200°C for 4 hours reaction time [84].

One of the value-added from this method is that glycerol can be obtained from the by-product of the transesterification process. As mentioned earlier, glycerol is the primary by-product from transesterification process, upon forming biodiesel. Therefore, to carry out glycerolysis, the by-product can be refined and recycled back as the reactant for the pre-treatment process. This phenomenon contributes profound impacts for waste mitigation and cost-effectiveness. Tu et al. studied the credibility of crude glycerol

extracted from the by-product of alkali transesterification process that producing biodiesel to treat grease trap collected from food industry. They reported that 1:1 mole ratio of oil to crude glycerol efficiently reduce 30% FFA of grease trap to less than 1% [85]. Previous work from Elgharbawy et al. reported the comparison of glycerolysis method by applying purified crude glycerol that is obtained from biodiesel production with pure glycerol [86].

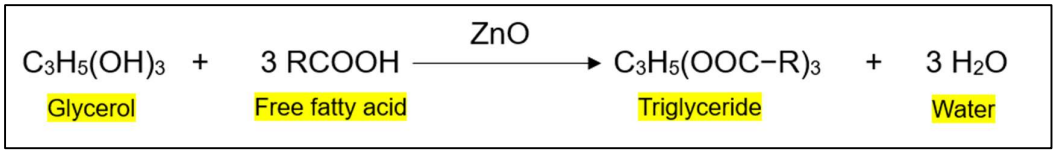


Figure 2.6 Reaction Equation Of Glycerolysis With Free Fatty Acid And Glycerol.

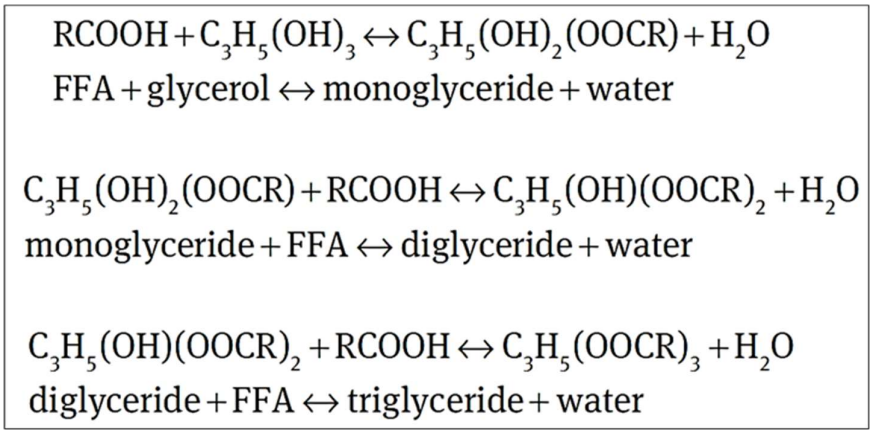


Figure 2.7 Reactions Formed From Glycerolysis Of Free Fatty Acid.

On top of that, it was recorded that the amount of glycerol produce as by-product via biodiesel production was approximately 10wt% of total yield of biodiesel. This event has caused in abundance amount of glycerol collected for every production of biodiesel. It was also reported that 66% of the amount of glycerol collected globally are from biodiesel industry [47]. Moreover, it was indisputable that there are substantial and excessive quantity of glycerol from various process and operational that has caused overflow of this component. There was interesting work studied by Kaur et al., discussing the valorization of crude glycerol obtained from biodiesel industry to value-added products to address the abundance issues of glycerol while tackling the economic and environmental issues [87]. Hence, it is coherent to overcome the abundance issue of glycerol by applying glycerol as the main element to treat the high amount of FFA in the SPO.

2.6.1 ZnO As Catalyst In Glycerolysis

Glycerolysis is recognized as relatively slow, high-temperature, and equilibrium-limited reaction that offer excellent efficacy in reduction of FFA in waste oils [88]. Hence, the application of catalyst is crucial as an aid to accelerate the rate of reaction and to enhance the transformation of reactants into the desired products. There are several types of catalyst that are generally employed in previous researches involving glycerolysis method, specifically to tackle the reduction of FFA problem in oil. The most common ones are heterogenous and homogenous types of catalyst. Heterogenous catalyst, that is catalyst that has different phase than the reactant (i.e. solid with liquid) and homogenous catalyst (i.e. liquid with liquid) are two different types of catalyst applied in glycerolysis.

Homogenous catalyst primarily utilizes alkaline catalyst such as KOH and NaOH as homogenous base catalyst that were utilized to enhance glycerolysis mechanism [48, 84, 89]. This type of catalyst offers high catalytic activity that contributes to fast reaction time and high stability. However, the drawback often involving the challenge in separation upon complete reaction [20]. On top of that, Maquirriain et al. studied the effectiveness of homogenous acid catalyst in glycerolysis method by using sulfuric, p-toluenesulfonic, and methanesulfonic acids to reduce FFA value [90]. Although the result is promising, this type of catalyst is not preferrable due to long reaction time, requires high temperature corrosive effects to the reactor and difficult to separate [91].

On the other hand, solid catalysts that are heterogenous type of catalysts offer numbers of advantages that contribute to significant result in glycerolysis reaction. Since the phases are distinctive, it offers easy separation that highly related to the convenient of the reaction. Furthermore, employing heterogenous catalyst is less corrosive, safer to handle and more compatible with equipment. High temperature tolerance also is a plus point when considering this type of catalyst, especially in glycerolysis [92].

One of the compelling types of heterogenous catalysts is metal oxides. They have significantly achieved excellent catalytic performance, high thermal stability, resistance to free fatty acids and water, and also highly reusability [93]. Metal oxides such as CaO [9] and MgO [94] were employed as heterogenous catalyst in glycerolysis method to reduce FFA significantly, prior to producing biodiesel. Previous study

reported the application of metal chloride as catalyst that is $SnCl_2.2H_2O$ achieved 97% FFA reduction conversion from high FFA content in cocoa bean [95]. Furthermore, these solid metals have advantageous properties that promotes catalysis pathway such as tuneable surface properties and chemical stability [96].

Other than calcium and magnesium, zinc is also one of the promising types of metal that able to reduce FFA. ZnO has caught attention as green catalyst for many applications due to its capability to promote eco-friendly chemical reactions and its potential for sustainable applications [97]. Comparing to other metals, zinc has low toxicity and is an essential trace element, rather than persistent pollutant. Hence, the application of zinc as catalyst is safe and environmentally benign [98]. The feature of heterogenous catalyst of ZnO contribute to the significance of easy separation that implied less wastewater treatment, less catalyst lost and no contamination of the product. Jansri studied the ability of many compounds of Zn such as Zn, $ZnCl_2$, ZnO and ZnSO4·7H2O as catalyst to reduce FFA in vegetable oil. It was reported that ZnO was able to reduce maximum of FFA while promoting triglyceride formation [99].

Moreover, due to its high stability, ZnO does not dissolve easily, resist to thermal degradation and maintains activity over multiple cycles. These qualities promote high reusability concept of this catalyst that is a plus point in various applications [100]. Other than that, ZnO offers high catalytic efficacy by acting as Lewis acid-base catalyst that provides good selectivity, yield and conversion with increasing the reaction rate and lower down the reaction time. This also indicate high FFA tolerance that is significant to the performance of glycerolysis. The mechanism involved when applying ZnO catalyst in glycerolysis is initiated from the catalyst function of surface Zn^{2+} ions acting as Lewis acid sites and surface O^{2-} ions acting as Lewis base sites. Initially, the carbonyl group of the excess free fatty acid in waste oil is adsorbed onto the ZnO surface, where the carbonyl oxygen coordinates with Zn^{2+}, increasing the electrophilicity of the carbonyl carbon and making it more susceptible to nucleophilic attack. Simultaneously, glycerol molecules interact with the basic oxygen sites on the ZnO surface, where an oxide ion abstracts a proton from a hydroxyl group. This leads to the mechanism of generating a nucleophilic alkoxide. Then, tetrahedral intermediate forms when the activated glycerol alkoxide attacks the activated carbonyl carbon of the free fatty acid. Subsequently, the intermediate collapsed. The synthesised of a new ester bond is then formed and release leaving group, producing monoglyceride, diglyceride or triglyceride. From the beginning to the end of the reaction, ZnO remains consistent,

because the Zn^{2+} and O^{2-} sites are regenerated after the reaction. This phenomenon contributes to the reusability of the catalyst. The dynamic between acid activation of the carbonyl and base activation of glycerol is the crucial element for the effectiveness of ZnO in glycerolysis. The enable factor is due to the efficient ester exchange under relatively mild conditions with minimal side reactions [101-103].

ZnO is also regarded as highly sustainable because it is naturally abundant, low cost, and high availability. Current study reported the successful study of zinc glycerolate in glycerolysis method prior to produce biodiesel [12]. To this date, there is only few studies implemented by other scholars of applying ZnO as catalyst in esterification. Hence, it is important to highlight the potential of ZnO in glycerolysis to accelerate the reaction by investigating the efficacy and effect to the reduction of FFA in oil.

2.6.2 Parameters Affecting Glycerolysis

There are numbers of previous researches applying glycerolysis method as attempt to reduce high FFA content in many types of oils. While applying the glycerolysis approach, there are few identified parameters that were exploited and controlled in order to obtain the optimum condition while assessing the effectiveness of the method. Table 2.6 reviews numbers of different parameters from previous studies that affecting glycerolysis reaction significantly and thus, influencing the reduction of FFA. Common parameters involved are temperature, type of catalyst, catalyst loading, molar ratio, residence time, and others.

Generally, gycerolysis reaction requires high temperature for effective reaction as to overcome the low solubility of glycerol into the oil. High temperature is necessary to ensure the performance of glycerolysis reaction, especially in higher range of FFA content of oil. Because waste oils exhibit high viscosity, higher temperatures are required during processing to reduce viscosity, improve fluidity, and enhance mass transfer. Felizardo et al. reported that the optimal temperature for glycerolysis is ranging from 180°C to 220°C [51]. However, it was notable that there was also a study reported the performance of glycerolysis using low temperature (65°C) to reduce FFA in jatropha oil from 4.54% to 0.06%. Although the outcome is impressive at this temperature, higher range of FFA value cannot accommodate to perform significantly at minimal

temperature [104]. Therefore, temperature with high values is crucial in performing glycerolysis method, especially in oil with elevated amount of FFA content.

On top of that, it is acknowledged that glycerolysis is commonly a slow process that acquire high kinetic energy to perform efficiently. Therefore, the addition of catalyst in glycerolysis is crucial to speed up the reaction and increase the rate of reaction by lowering the activation energy and provides alternative pathway to facilitate the product conversion. Hence, selection of catalyst is influential to acquire optimal glycerolysis reaction [9]. Ideal concentration of catalyst is also important to ensure the catalyst is consumed wisely to optimize the operating cost.

One of the most vital parameters that influence the productivity of glycerolysis is molar ratio. Typically, three moles of FFAs are required to form with one mol of glycerol in order to obtain triglyceride. Therefore, it is significant to identify the optimum molar ratio in the glycerolysis method for the mechanism to work successfully. Moreover, since the reaction is reversible, it is also crucial to remark that excess of glycerol is needed to hinder the reaction to shift to the right [90]. Different conditions applied performed distinctively depending on the type of oils. These parameters are correlated and influential to one another. As example, high temperature with high catalyst loading gives better result compared to low temperature with low catalyst loading. However, it is critical to determine the ideal condition that offers high FFA conversion while considering the economical point of view.

To this date, there are few studies related to application of glycerolysis for esterification derivation for several oils. However, there is no work reported on the application of glycerolysis for SPO prior to synthesis of biodiesel. On top of that, the feasibility of ZnO as catalyst to enhance glycerolysis reaction has not been studied. Therefore, in this study, SPO will be treated by glycerolysis with the aid of ZnO to reduce the FFA before producing biodiesel through transesterification method.

Table 2.6
Previous Studies Of FFA Reduction By Glycerolysis Method

Feedstock	Parameters condition	Initial FFA value (%)	Final FFA value (%)	FFA reduction efficiency (%)	Optimum condition	Reference
Waste cooking oil	Temperature: 65 ℃, Oil to glycerol mol ratio: 1:1, 1:2 and 1:3, Catalyst NaOH concentration: 0.875, 1.3 and 1.75 %-w of oil	6.1	0.46	92.4	Oil to glycerol mol ratio: 1:3, Catalyst NaOH concentration: 1.75 %-w of oil	[105].
Sunflower oil	Temperature: 60‑180 ◦C, Residence time: 30 - 120min, CaO catalyst amount: 0.4‑0.6 wt (g/g)), Glycerol to Oil ratio: 1‑1.5.	48.58	0.98%	97.8%	Temperature: 170 ◦C Residence time: 39.9 minutes CaO catalyst: 0.591wt (g/g) Glycerol to oil ratio: 1.026 g/g	[9]
Soybean oil	Temperature: 120 – 159 ◦C SBA-15 functionalized catalyst wt (%): 0.6, 1.2, 2.0 and 3.0 FFA: Glycerol ratio: 1:1, 1:3, 3:1 Residence time: 6 hours	90	0.44	99%	Temperature: 159 ◦C. SBA-15 functionalized catalyst wt (%): 3.0 FFA: Glycerol ratio: 1:3	[106]
Used cooking oil	Temperature: 70 ℃ KOH catalyst wt (%): 0 – 1.6 Glycerol wt (%): 0 – 200% Residence time: 10 – 60 minutes	7.6 and 11.97	<1	99%	KOH catalyst wt (%): 1.6, Glycerol wt (%): 100, Residence time: 30 minutes	[86]

Feedstock	Parameters condition	Initial FFA value (%)	Final FFA value (%)	FFA reduction efficiency (%)	Optimum condition	Reference
Raw grease trap	Temperature: 200, 215, 230°C Residence time: 10 – 240 minutes FFA: glycerol ratio: 0.5-2.0 M	30	<1%	99	Temperature: 230°C Residence time: 150 minutes FFA: glycerol ratio: 1.1 M	[85]
Palm waste oil and fish waste oil	Pure and crude glycerol Glycerol: 50 – 100 wt% Residence time: 5 - 60 minutes	2.8 2.0	0.4	80	Crude glycerol Glycerol: 100 wt% Residence time: 30 minutes	[6]

CHAPTER 3
RESEARCH METHODOLOGY

3.1 Introduction

In this chapter, the thorough step-by-step methodology were presented and explained. The overall methodology was as shown in Figure 3.1 in comprehensible manner. The procedures are divided into three phases which are: (1) characterization of SPO, (2) glycerolysis of SPO and (3) production of biodiesel which coherently related to the three main objectives.

Firstly, SPO was characterized into two categories which were physical and chemical characteristics. The characterization was performed to analyze the feasible of SPO to become a potential biodiesel feedstock. After that, the results obtained were compared with crude palm oil, one of the typical biodiesel feedstocks to discuss the similarities and differences as well as to nominate the capability of SPO to derive biodiesel. After that, glycerolysis process was executed with different parameters that were temperature, catalyst loading and SPO to glycerol molar ratio. This reaction was done to investigate the reduction of FFA in SPO using glycerolysis and to obtain the optimal condition for esterification by glycerolysis method in SPO. Each parameter was performed with different values as shown in Figure 3.1 by acquiring their FFA values. The amount of FFA in SPO for each parameter was analyzed for every hour in 3 hours. Upon obtaining the oil with the lowest FFA value, biodiesel was then produced and analyzed.

3.2 Materials

SPO was collected from cooling pond to obtain the maximum FFA from palm oil milling effluent in Kemaman Palm Oil Mill, Terengganu. CPO was collected from Kemaman Palm Oil Mill, Terengganu with 99% purity. Other chemicals with their details were as shown in Table 3.1.

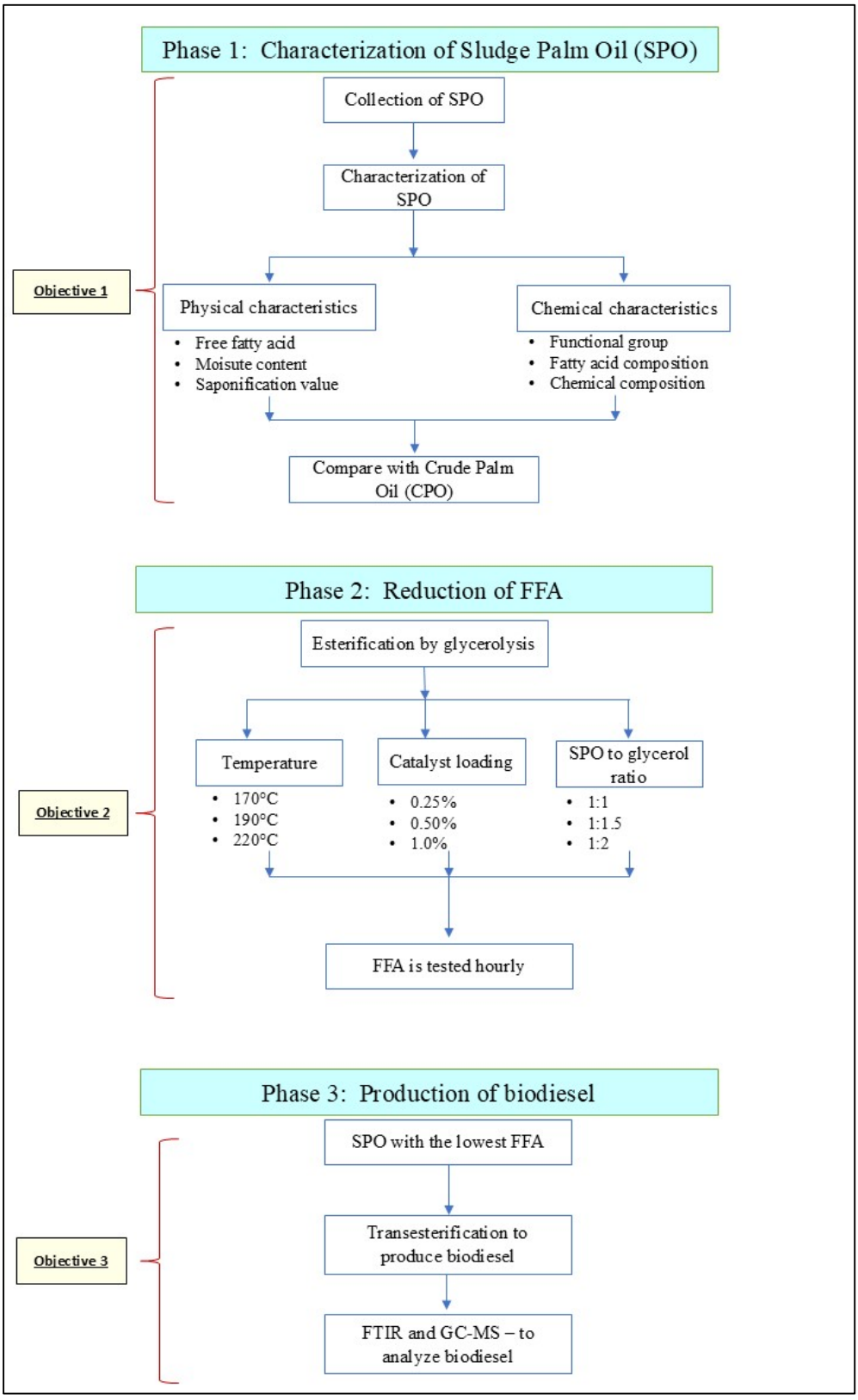


Figure 3.1 Overall Methodology Of The Study.

Table 3.1
Chemicals That Were Utilized In This Study.

Chemical	Brand	Purity (%)	Remarks	Usage
Sludge palm oil	-	-	-	3.2 kg
Crude palm oil	-	99	-	10 mL
Pure glycerol	Systerm	99.7	-	600 g
Sodium hydroxide	Systerm	-	0.1M	250 mL
Phenolphthalein indicator solution	Bendosen	1	-	13 mL
Isopropyl Alcohol	Systerm	>99	-	13 L
Zinc Oxide	Systerm	>99%	In powder form	18.2 g
Ethanol	HmbG Chemicals	99.9%	-	210 g
Potassium Hydroxide	R&M Chemicals	-	In pallet form	45 mL
Potassium hydroxide	R&M Chemicals	-	1.0 N, in liquid form	6 g
Hydrochloric Acid	Systerm	-	0.5N	50 mL

3.3 Collection Of SPO

SPO was collected from the waste water treatment plant in Kemaman Palm Oil Mill, Terengganu. The palm oil milling effluent produced from the factory mainly undergo several processes in the treatment plant before being discharged to the designated watercourse or land.

SPO was collected in the cooling pond, the first treatment pond for SPO to be discharged from the palm oil mill. The oil was collected at the upper part of the pond to accumulate the most oily part, and avoid the element of water and moisture. An amount of 4 litres of SPO were collected in specimen bottle. The sample was stored in the lab at cold temperature ranging 10 to 16°C to avoid deterioration. Before performing any evaluation, the SPO was heated to 65°C to change its phase from semi-solid to liquid as shown in Figure 3.2.

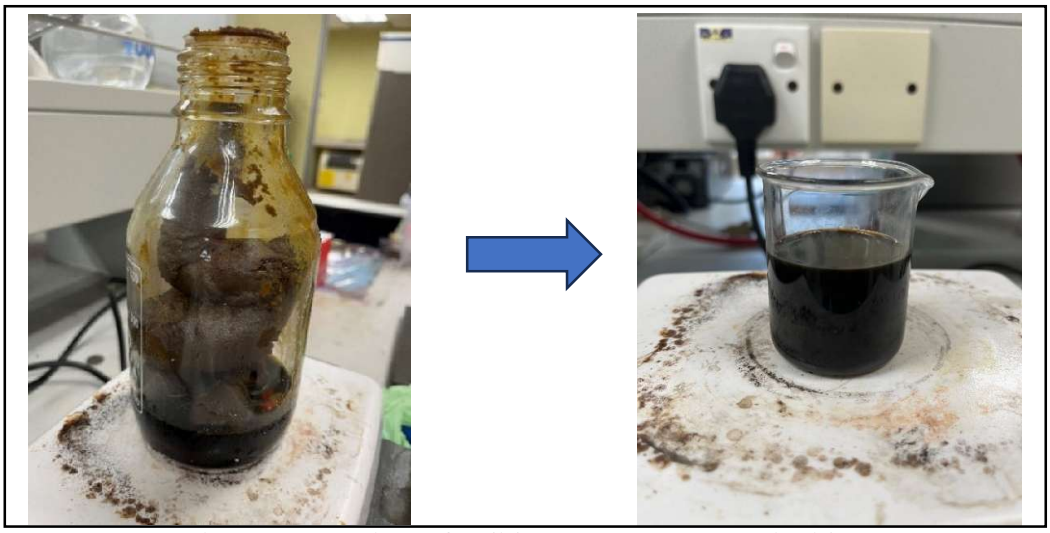


Figure 3.2 Heating Of Solid SPO To Turn Into Liquid

3.4 Characterization Of SPO

SPO in liquid form was then been analyzed for its characterization. Physical characterization of SPO for this study include FFA, moisture content and saponification value. On the other hand, chemical characterization comprises of functional group, fatty acid composition and chemical composition. The significance of each characterization is thoroughly explained in the next section. Each characterization was then also been carried out on CPO to compare the similarities and differences on the characteristics of SPO.

3.4.1 Free Fatty Acid (FFA)

The value of FFA of collected SPO is important to analyze as it indicates the deterioration level of the oil. In fact, for this study, it is needed to acquire the FFA value prior performing any pre-treatment method (i.e., glycerolysis) so it can be compared afterwards. The method employed for the test is titration method referring to American Oil Chemists' Society (AOCS) (1989) method Ca 5a–40 [107]. Approximately 0.5 to 0.6g of SPO sample was weighed in 10mL beaker using weighing scale. The reading was then recorded. Next, the sample is diluted with 50mL of isopropyl alcohol (IPA) in a conical flask and shaken well. 50µL of 1% of phenolphthalein indicator was then dropped inside the mixture as an indicator and shaken well. A retort stand clamped with 50mL burette filled with NaOH was set up for titration. After that, the sample was then

titrated by slowly opening the stopcock to drop the NaOH. The set-up for FFA test was as shown in Figure 3.3. The sample was titrated until the mixture turns light pink. The reading of the NaOH dropped was recorded. Equation (3.1) displayed the calculation to obtain the FFA value. 25.6 was the equivalence factor for the dominant fatty acid in palm oil which is palmitic acid [108]. The procedure was repeated three times to get the average value.

$$\text{FFA}\ (\%) = \frac{\text{V x N x } 25.6}{\text{W}} \tag{3.1}$$

where; V = Volume of titrant, mL

N = Normality of titrant

W = Weight of sample, g

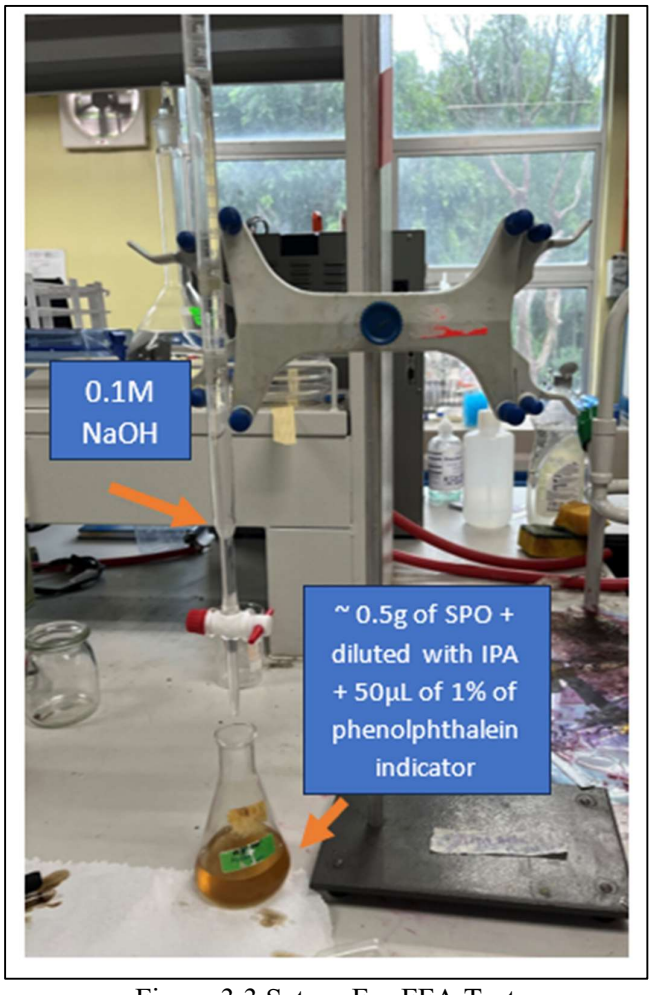


Figure 3.3 Set-up For FFA Test

3.4.2 Moisture Content

It is important to minimize the moisture content in oil as it is viewed as contaminant that may disrupt further oil application. On top of that, moisture content was a crucial factor that reflects the quality and efficiency of the oil. For this study, to understand the characteristics of SPO, moisture content was measured by using air oven method that is based on AOCS (1997) official method Ca 2c–25 [109]. The fundamental for the estimation of the moisture content was the weight loss of the sample at the end of drying process. Firstly, the weight of empty aluminium dish was first recorded as W1. Upon placing the aluminium dish on the weighing scale, approximately 5g of the oil sample was poured and the weight was recorded as W2. The oil sample was put inside the oven and the temperature was set at 101°C. The application of this temperature set is to dry out the water content within the oil. After the oven has reached its process value of 101°C, the drying process started. After 30 minutes, the sample was then taken out from the oven and allowed to cool down to room temperature in a desiccator. The weight of the dried sample was recorded as W3 before putting it back to the drier for further drying. The procedure then repeated until the loss in weight does not exceed 0.05% per 30 minutes drying period. The moisture content was then calculated using Equation (3.2). The procedure was repeated three times to get the average value.

$$\text{Moisture content (\%)} = \frac{\text{W2} - \text{W3}}{W2 - W1} \text{ x } 100\% \qquad (3.2)$$

3.4.3 Saponification Value (SV)

Saponification value (SV) stipulates the amount of alkali required to saponify the oil. Oils with lower level of SV usually have higher degree of unsaturation. For this characterization, the method was adapted as similar as reported work from Mohamad et al. [110]. 1g of oil sample was firstly weighed before being transferred in a 100mL round bottom flask. Next, 1.0N of KOH was prepared for the next step. The oil sample was mixed with 15mL of the prepared KOH and 10mL of distilled water in the round bottom flask before being boiled at 100°C and stirred uniformly. The mixing process was left for a duration of 1 hour. After that, the mixture was then titrated with 0.5N of

Hydrochloric Acid, with the aid of 1% phenolphthalein as indicator. The procedure was repeated for the blank sample, that is without the oil. The saponification value was then calculated by applying Equation (3.3). 56.1 is the molecular weight of KOH [110].

$$\text{Saponification value (SV)} = \frac{(V_b - V_s)\text{x N x } 56.1}{W} \quad (3.3)$$

where; V_b = Volume of blank, mL

V_s = Volume of titrant, mL

N = Normality of titrant

W = Weight of sample, g

3.4.4 Functional Group

It is important to identify the functional group in SPO to justify the feasibility of SPO to produce biodiesel. The procedure was to recognise the presence and absence of functional group when compared to the typical biodiesel feedstock. Mainly, functional group characterization was carried out by using Perkin-Elmer model Fourier transform infrared spectroscopy (FT-IR) spectrometer equipped with attenuated total reflectance (ATR). The model capable of covering the spectral range of 4000 cm^{-1} to 400 cm^{-1}. This method needs the absorption of infrared light wavelength from the oil. A drop of 2 µL of sample was first spotted on the plate [70]. The transmittance of the wavelength was then plotted. Functional group of the sample was then analyzed by observing the transmittance peaks.

3.4.5 Fatty Acid Composition

The motive to analyze the composition of fatty acid in SPO was to identify the presence and composition of types of saturated and unsaturated fatty acid in the oil. The analysis was significant as it influences the characteristics of the biodiesel produced. The composition will be analysed by using Gas Chromatography (GC) (Shimadzu GC-17A) with a capillary column BPX 70 (30m x 0.25mm x 0.25 µm) and an FID detector. The analysis was outsourced to external accredited laboratory with following procedure. Sample preparation was required to increase the volatility in the oils for

efficient analysis. The sample was first converted to fatty acid methyl ester (FAME). Approximately 50 mg of SPO was transesterified using methanolic KOH, with methyl heptadecanoate (C17:0) added as an internal standard. The resulting FAMEs were extracted into hexane, dried over anhydrous sodium sulfate, and analyzed by GC–FID. GC analysis was performed on a capillary column suitable for FAME separation. The programmed temperature was at 120 °C, with an increment of 3°C per minute up to 245°C, while the injector and detector temperature were set at 260 °C and 280 °C respectively. High purity helium gas (99.99 %) act as the carrier gas with a flow rate of 0.3 mL/min. The fatty acid peaks were then will be classified and quantified by comparatively analyzing their peak areas and retention times with those of standard fatty acid [70]. The percentage of saturated and unsaturated of fatty acid was then observed and compared.

3.4.6 Chemical Composition Profile

This characterization was to analyse the chemical composition presented in the oil. The analysis was performed by GC-MS (Gas Chromatography-Mass Spectrometry) method using GC-MS Perkin Elmer Clarus 600. The analysis was outsourced to external accredited laboratory with following procedure. Sample preparation was required to increase the volatility in the oils for efficient analysis. The sample was first converted to fatty acid methyl ester (FAME). Approximately 50 mg of SPO was transesterified using methanolic KOH, with methyl heptadecanoate (C17:0) added as an internal standard. The resulting FAMEs were extracted into hexane, dried over anhydrous sodium sulfate, and analyzed by GC–MS. Elite-5MS capillary column was applied as the chromatographic column with dimension of 30m length, 0.25mm diameter and film thickness of 0.25 µm. The injection sample volume was 1 µL. Phase reference was according to 5% diphenyl and 95% dimethyl polysiloxane (low bleed). Temperature limit was set at 70 to 325°C. The oven temperature program was set as follow: initial temperature 60°C for 2 minutes, ramp 1 at 10°C/min to 200°C, ramp 2 at 3C/min to 230°C (hold 5 minutes), ramp 3 at 10°C/min to 300°C (hold 10 minutes). The carrier gas was helium. The transfer line between GC and MS was set at 280°C. Compounds were identified by comparison of their mass spectra with entries in the NIST 20 mass spectral library and by retention time matching with reference standards where available. The peaks review was then analyzed to obtain the component present within

the oil [111].

3.5 Characterization Of Crude Palm Oil (CPO)

All the characterization analysis was then repeated with using CPO sample instead. This method was done to compare the similarities and differences of the SPO to CPO. The comparison was then discussed and deduced to analyze the capability of SPO to replace CPO on becoming biodiesel feedstock.

3.6 Esterification By Glycerolysis

The pre-treatment method of SPO to reduce the FFA was performed by glycerolysis. Basically, this procedure is the primary and crucial part of this study. This approach reflects on the main objective of this research that was to validate the feasibility of glycerolysis to lower down the amount of FFA on oil and to evaluate the effects for each parameter in glycerolysis to the reduction of FFA.

Esterification by glycerolysis was carried out in a 250mL conical flask with an attached condenser, similar to previous study by Cai et al. The set-up for the procedure was as shown in Figure 3.4. Firstly, desired amount of glycerol was heated in the conical flask on a heating plate. This step was to increase the kinetic energy of the particles within the glycerol to react with the upcoming the free fatty acid in SPO. Upon reaching 65°C, designated amount of SPO was added inside the flask. Magnetic stirrer was used to ensure thorough and uniform mixing at 300rpm. Thermometer was installed as a tool to monitor the temperature within the reaction. Once the desired temperature reached, the assigned amount of powder ZnO was added. The mixture was allowed to heat to specified temperature and once the set temperature was achieved, the experiment begins and proceeded for 3 hours. Using a glass pipette, the mixture was taken out for every hour for approximate 3 to 4 drops to test for its FFA by titration method, similar to previous mentioned procedure. The FFA reading was recorded for every hour in 3 hours. In order to ensure that the formation of water upon esterification will not favour hydrolysis, condenser was installed at the top of the flask to absorb out the water formed from the reaction.

Figure 3.4 Glycerolysis Set-Up

The process was repeated using different parameters as stated in Table 3.2 to investigate the influence of each parameter to the reduction of FFA. On top of that, the aim was also to obtain the ideal parameter that is capable to reach low FFA value that was acceptable for biodiesel production. The range value for each parameter was determined by referring to previous studies [83, 90, 95, 112].

Table 3.2
Different Parameter Applied For Glycerolysis Method

Parameter	Values
Temperature (°C)	170, 190, 220
Catalyst loading (wt%)	0.25, 0.5, 1.0
SPO to glycerol mol ratio	1:1, 1:1.5, 1:2

The justification for the values selected were as follow. It was known that glycerolysis required high temperature, especially when the native SPO contain high amount of FFA. Temperature at 150 to 160°C were able to reduce FFA significantly with the range of 90% conversion, but with lower range of initial FFA values [6, 113]. Due to the higher amount of FFA in this study (59%), it was presumed that temperature lower than 170°C is inefficient due to the elevated FFA value of collected SPO. On the other hand, it was studied that temperature higher than 220°C is invalid in glycerolysis as it may burnt the oil and disrupt the process entirely [51, 89]. Hence, 220°C would be the temperature limit to acquire significant result in the performance study. Therefore, a range set of temperature between 170°C to 220°C were relevant and ideal

to be investigated to the performance of glycerolysis. For this study particularly, 170°C, 190°C and 220°C were selected as the main variables for different temperature because of its significance.

Additionally, in glycerolysis, catalyst loading lower than 0.25 wt% does not give significant effect as the quantity is inadequate to facilitate the reaction [114]. On the other hand, higher than 1.0wt% of heterogenous catalyst may disrupt the homogeneity in the reaction. Therefore, range between 0.25wt% to 1.0wt% were selected as parameters for this study [83]. Furthermore, distinctive mol ratio gives different significant effect. Basically, in order to derive 1 mol of triglyceride from FFA, 3 mol of FFA within the SPO is needed to react with to 1 mol of glycerol. It is important to note the essential of excess glycerol to facilitate the reaction. Hence, following parameter for mol ratio were selected to be analyzed to observe the significant differences as shown in Table 3.3. Since this study applying the reaction to favor the formation of triglyceride, mol ratio with 1:1 indicated the general reaction of 3 mol of FFA with 1 mol of glycerol that implies the absence in excess of glycerol. On the other hand, at 1:1.5 mol ratio indicated 50% of excess glycerol while 1:2 implying 100% of excess glycerol. These distinctive mol ratios were significant to investigate the individual performance in affecting the glycerolysis reaction. It was important to note that mol of FFA was based on palmitic acid, that was the primary fatty acid in SPO.

Table 3.3
Justification For Different Mol Ratio In This Study.

Mol ratio	Justification
1:1	Determined as no excess of glycerol while favoring the formation of triglyceride that is 3 mol of FFA to 1 mol of glycerol.
1:1.5	Implied as 50% of excess glycerol.
1:2	Implied as 100% of excess glycerol.

The experiment was conducted by maintaining two variables while varying one parameter. As example, at temperature 170°C and catalyst loading 0.25%, the SPO to glycerol mol ratio is varied at 1:1,1:1.5, and 1:2 to perform glycerolysis. Table 3.4 displayed the actual values of the sample for catalyst loading and SPO to glycerol mol ratio for better insight to this study. The experiment was repeated three times to obtain the average values. The final FFA reduction was calculated referring to Equation 3.4.

Table 3.4
Actual Values Of SPO, Glycerol, And ZnO For Each Parameter

Catalyst loading (%)	SPO to glycerol mol ratio	SPO (g)	Glycerol (g)	ZnO (g)
0.25	1:1	38.4	4.6	0.096
0.25	1:1.5	38.4	6.9	0.096
0.25	1:2	38.4	9.21	0.096
0.5	1:1	38.4	4.6	0.192
0.5	1:1.5	38.4	6.9	0.192
0.5	1:2	38.4	9.21	0.192
1.0	1:1	38.4	4.6	0.384
1.0	1:1.5	38.4	6.9	0.384
1.0	1:2	38.4	9.21	0.384

$$\text{FFA reduction (\%)} = \frac{\text{FFA2} - \text{FFA2}}{\text{FFA1}} \text{ x } 100\% \quad (3.4)$$

where; FFA1= Initial FFA value (%)

FFA2 = Final FFA value (%)

3.7 Production Of Biodiesel

After performing glycerolysis for each parameter, the sample of treated SPO with the lowest FFA achieved was taken for further experiment. This treated SPO was selected as the best candidate to transform into biodiesel by performing transesterification method. Transesterification process was performed by first heating up the treated SPO on a heating plate at 70°C to ensure SPO is in liquid phase. Ethanol was used as the important reactant for this process instead of methanol due to numbers of reasons. Ethanol offers numbers of advantages including (1) higher solubility in oil that helps in enhancing the reaction, (2) can be acquired from renewable source that promotes sustainability and (3) safer and cleaner since it is non-toxic [43]. Mol ratio of 15:1 of ethanol to SPO was applied as excess amount of ethanol was required. This particular value was selected and applied in the present study after reviewing previous research findings regarding the optimal conditions for biodiesel production using ethanol [115-117]. The definite values of each element were demonstrated as in Table 3.5.

Table 3.5.
Actual Values Of SPO, Ethanol And KOH For Transesterification Method.

Component	Parameter	Value (g)
SPO	15:1 mol ratio of ethanol to SPO	25.6
Ethanol	15:1 mol ratio of ethanol to SPO	69.11
KOH	2wt%	1.79

Upon heating the treated SPO, accurate amount of SPO and ethanol were weighed before being added as mixture in a 250mL Erlenmeyer flask. A speed of 300rpm was maintained inside the flask by using magnetic stirrer. Thermometer was used to monitor the constant temperature of 70°C. KOH was typically used as the catalyst to enhance the rate of reaction of alkali-catalyzed transesterification. Basically, 2 wt% of KOH was added to the mixture after the mixture reached 70°C. The 2wt% value was selected when introducing KOH catalyst as suggested by previous report [46, 63]. The reaction was then carried out for 3 hours under constant speed and temperature.

After 3 hours, the mixture was allowed to cool down to room temperature. Next, the mixture was carefully transferred into a separating funnel, clasp to a retort stand. This step was to allow separation of pure biodiesel and other component by exploiting gravity effect. The mixture was then allowed to be separated for 24 hours. The upper part was then taken as the biodiesel product while the lower part was removed. The transesterification method was performed similarly to previous study [3, 42, 118].

3.7.1 Analysis Of Biodiesel

The produced biodiesel was then been analyzed for its authentication and to verify the success of this study. The collected biodiesel was analyzed by utilizing two characterization methods which were: Fourier-transform infrared spectroscopy (FTIR) and using gas chromatograph-mass spectrometry (GC-MS).

3.7.1.1 FTIR Method To Analyze Biodiesel

In this research particularly, Fourier-transform infrared spectroscopy (FTIR) method was applied to authenticate the production of biodiesel. The presence of ester functional group in the produced oil verifies the production of biodiesel. This analysis was performed similarly as previous FTIR test by using Perkin-Elmer model FTIR

spectrometer equipped with attenuated total reflectance (ATR). The model capable of covering the spectral range of 4000 cm^{-1} to 400 cm^{-1}. This method needs the absorption of infrared light wavelength from the oil. A drop of 2 µL of sample was first spotted on the plate [70]. The transmittance of the wavelength was then plotted. The functional group as well as bond types were then acquired from the analysis of the transmittance graph.

3.7.1.2 GC-MS Method To Analyze Biodiesel

The analysis was performed by GC-MS (Gas Chromatography-Mass Spectrometry) method using GC-MS Perkin Elmer Clarus 600. Elite-5MS capillary column was applied as the chromatographic column with dimension of 30m length, 0.25mm diameter and film thickness of 0.25 µm. The analysis was outsourced to external accredited laboratory with following procedure. Sample preparation initiated when produced biodiesel at 100 mg was diluted thoroughly with n-hexane in 10mL volumetric flask. Addition of 100 µL of ethyl heptadecanoate was appropriate as internal standard solution. The injection sample volume was 1 µL. Phase reference was according to 5% diphenyl and 95% dimethyl polysiloxane (low bleed). Temperature limit was set at 70 to 325°C. The oven temperature program was set as follow: initial temperature 60°C for 2 minutes, ramp 1 at 10°C/min to 200°C, ramp 2 at 3°C/min to 230°C (hold 5 minutes), ramp 3 at 10°C/min to 300°C (hold 10 minutes). The carrier gas was helium. The transfer line between GC and MS was set at 280°C. The samples prepared were placed in an ultrasonic bath for 5 min to accelerate the dissolution. Compounds were identified by comparison of their mass spectra with entries in the NIST 20 mass spectral library and by retention time matching with reference standards where available. The peaks review was then analyzed to obtain the component present within the produced biodiesel [111]. The validation of success biodiesel formation was analyzed when FAEEs were formed.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Introduction

After reviewing previous literature works and constructing the methodology for the whole research, this chapter conduces the climax of this study to present the output and significant findings. In this chapter, all the detailed results obtained from the constructed procedures are presented. The findings are discussed and evaluated to achieve the objectives and to deduce the study.

4.2 Physical Characterization Of SPO And CPO

Both SPO and CPO were characterized respectively and compared thoroughly. From the initial observation, the features of SPO were opposed to that of CPO. By referring to Figure 4.1, the difference between SPO and CPO were apparent as displayed from the physical features. SPO was observed as semi-solid oil in room temperature with dark brown colour while CPO was in liquid phase and in the lighter shade of brown colour. Both oils have very distinctive odour. SPO has this smelly, strong, and tangy odour that is similar to previous work reported by Loh et. al. [15] while CPO has more to neutral and slight nutty odour.

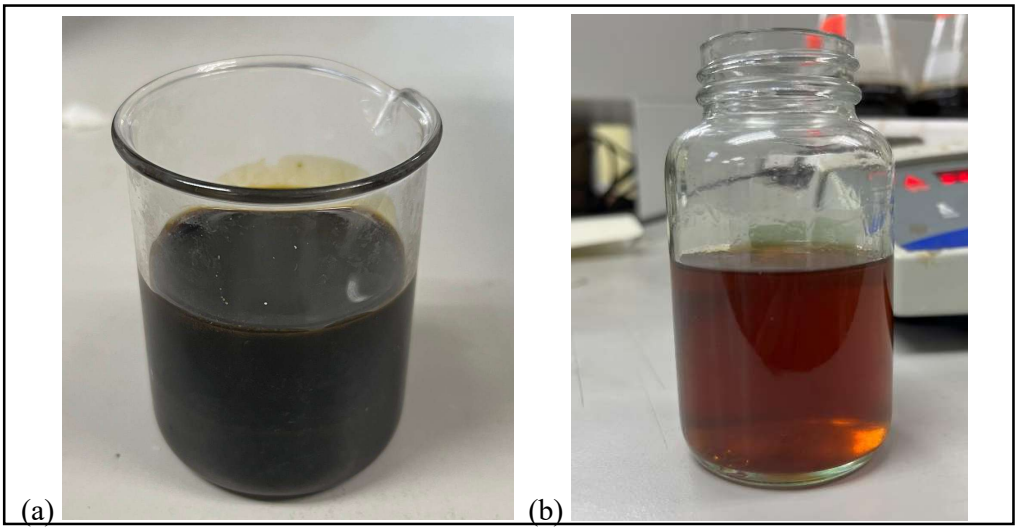
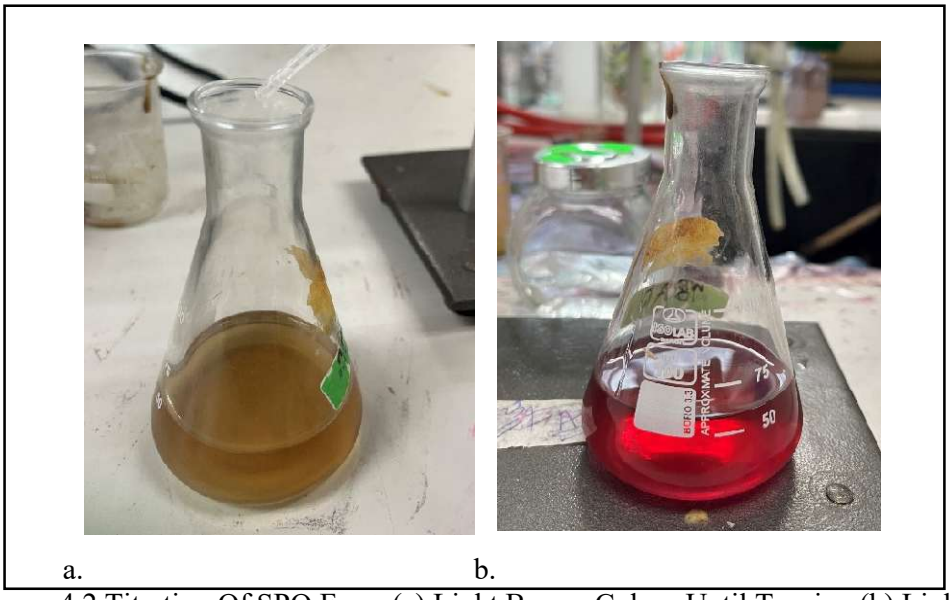


Figure 4.1 Physical Feature Of (a) SPO And (b) CPO.

4.2.1 Free Fatty Acid (FFA)

The FFA for both oils were tested by applying titration method with NaOH. Diluted SPO was titrated with NaOH to neutralize the presence acid until the mixture turns into from light brown to light pink (Figure 4.2). Table 4.1 displays the FFA value for both oils and other physical characterization. Upon testing, the FFA value acquired from the SPO collected in this study was assessed to retain a total of 59% of FFA. When comparing, the value of FFA in this particular study was impactfully higher than the value of FFA for typical SPO that have been reported in previous related researches [37, 119]. For instance, a study from Indonesia palm oil mill explored SPO with 36.7% of FFA while other researcher in Malaysia discovered SPO with around 23% of FFA value [73]. On top of that, a study from Fong et al. assessed SPO from different origins with high FFA amount ranging from 12% to 87% [14].



a. b.

Figure 4.2 Titration Of SPO From (a) Light Brown Colour Until Turning (b) Light Pink.

High content of FFA can be contributed from following factors that include long exposure in treatment pond due to triglyceride hydrolysis and during milling process from palm oil production. The elevated amount of FFA in SPO reflected that SPO has low quality of oil, and consequently was treated as waste. [14, 69]. On top of that, collected SPO in this study was obtained from the cooling pond which was the early part of the treatment plant. Hence, the high FFA value was as predicted as there was no treatment process has been done yet.

Raw materials with high FFA content were not recommended for production of biodiesel. In this study particularly, the majority composition in the SPO was free fatty acid, that was not suggested to become the main feedstock for biodiesel. It was reported that there was up to 59% of FFA in SPO that should be reduced to 3% or lower in order to become feasible to form fatty acid alkyl ester that is biodiesel. These free fatty acids should be transformed into glycerides, that would be the main constituents when associated with production of biodiesel through transesterification. Hence, employing SPO directly to forming biodiesel without pre-treatment was not viable.

On the other hand, CPO tested in this study was inspected to contain very low FFA amount, compared to SPO. The reported amount of FFA in the CPO was only 0.2%. The minimal value was similar to previous works reported [120, 121]. According to the Malaysian standard of CPO, FFA content in the oil should be lower than 5% [70]. Therefore, this value was as anticipated because CPO contains very minimal impurities and the constituents existed were mostly triglycerides and other glycerides. This feature was the theoretical reason why CPO can be directly regarded as the primary biodiesel feedstock without any treatment required.

Table 4.1
Physical Characteristics Of SPO And CPO.

Characteristics	SPO	CPO
FFA (%)	59	0.2
Moisture (%)	1.96	0.24
Saponification value (mgKOH/g)	214.5	197.1

It was evident and conceptual that the difference of FFA value between both oils were very high due to the nature of the oils. Since FFA is one of the indications of the quality, performance, and degree of deterioration of oil, high value of FFA in SPO implied low quality of the oil. Furthermore, the FFA level for SPO in this study was considered in the higher range when compared to other reported literatures. Hence, this SPO was low in quality, high in deterioration tendency and possibly recalcitrant to be treated [37]. The high content of FFA in the SPO was highly undesirable and required to be reduced for further process in producing biodiesel. Therefore, this study examined the treatment of identified SPO by applying glycerolysis that will be discussed in the next sections.

4.2.2 Moisture Content

The amount of dissolved water presence in the oils was presented as moisture content. Excess amount of moisture in oils were related to the quality of oil and also influenced by the FFA value of oils [122]. Table 4.2 shows the values of moisture content for each oil by applying air oven method where periodic drying process of samples took place until the weight loss was minimal. The procedure stopped at 120 mins as the changes of weight of dried sample was relatively low to the previous value. According to the result obtain, moisture content of SPO collected for this study was at 1.96%.

Table 4.2
Moisture Content For SPO And CPO.

Time (min)	W1 (g)	W2 (g)	W3 (g)	Moisture content (%)
SPO				
30	1.9355	4.0812	4.0624	0.88
60	1.9355	4.0812	4.0446	1.70
90	1.9355	4.0812	4.0411	1.87
120	1.9355	4.0812	4.0391	1.96
CPO				
0	1.9284	3.9035	3.8990	0.23
30	1.9284	3.9035	3.8984	0.26
60	1.9284	3.9035	3.8988	0.24

W1= Empty aluminium dish, W2= weight of sample before entering dryer, W3= weight of dried sample

This value was affected by the value of FFA as reported by previous work by Emebu et al. that stated moisture content, temperature and storage time of palm oil affecting the value of FFAs and vice versa [122]. Recent study recorded physical characteristics of high value of FFA in waste cooking oil. The value of FFA reached 14% when the moisture content was 2.3% [123]. There was also a study reported that moisture can go up to 10% when the FFA content in the oil was 77% [14].

High value of moisture content in SPO in this study was predictable due to the high deterioration of oil. Furthermore, the collected waste in the treatment pond consists of processed palm oil that has through numbers of processes that contribute to the water content in the oil. Storage condition, washing process, hydrolysis process and

environmental factors promotes the moisture content in palm oil mill [124]. It was notable that the excess moisture in the oil was not favorable, especially to be applied as biodiesel feedstock. Thus, treatment of SPO was required to lower down the water content in the oil to elevate the quality of the oil.

Conversely, the drying process for CPO stopped at 60 mins since there were no significant changes on the weight of the dried sample in the early period. The moisture content for the tested CPO was relatively low which was 0.24%. According to Malaysian standard of crude palm oil, the acceptable value of moisture content was lower than 0.3% for further application [70]. Other researches recorded moisture content of CPO in the range of 0.2 – 0.5% [122, 125]. Prominent differences of moisture content between SPO and CPO were due to the gap of quality and deterioration of oil. Furthermore, excess amount of water in the SPO was highly not recommended, especially when composing biodiesel. Since FFA and moisture content were highly linked and correlated between each other, the significant reduction of moisture content was evident when FFA was reduced significantly [122]. Therefore, reducing the amount of FFA is crucial to overcome the elevated moisture content in the oil.

4.2.3 Saponification Value (SV)

SV was directly linked to the amount of base needed to saponify the samples that are CPO and SPO. Furthermore, the value of SV was reported as a quality index that correlate with the molecular weight of the triglycerides in the oil. Based on the result acquired in this study, it was reported that SPO has slightly higher SV compared to CPO. The value of SV for CPO was determined at 197.1 mgKOH/g. The value acquired for CPO in this study corresponded with the expected rate. The SV of CPO typically ranges from 195 to 209 mg KOH/g, reflecting its relatively high proportion of long-chain fatty acids. This lower SV indicates fewer moles of fatty acids per gram of oil, consistent with the predominance of triglycerides containing longer carbon chains, such as palmitic and oleic acids [126].

In contrast, the SV of the SPO collected from the cooling pond was determined to be 214.5 mg KOH/g. This elevated SV suggests a higher proportion of shorter-chain or free fatty acids in the waste oils. Since the FFA value of collected SPO was definitely on the higher side, the substantial value of SV was anticipated. Furthermore, the probable basis to this value is may be due to the hydrolysis or degradation processes

occurring during oil recovery and handling in the milling process. On top of that, it was indisputable that oils with high SV are more suitable to produce soap. The underlying factor to this is because of it signifies a higher proportion of shorter-chain fatty acids, that react more readily with lye to form soap. It was acknowledged that some portion of produced SPO from the milling process were utilized to produce cheap soap if not discarded. Therefore, the elevated value obtained from the SPO in this study indicated that SPO has higher content of shorter-chain fatty acids, making it ideal for soap formation.

Given that triglycerides serve as the primary constituents in the transesterification process for biodiesel production, oils exhibiting lower SV were considered more suitable as feedstock. A lower SV typically indicates the presence of longer-chain fatty acids and a reduced proportion of free fatty acids, which not only enhances the yield of biodiesel but also minimizes the formation of soap during processing. This contributes to a more efficient conversion process, reduced catalyst consumption, and improved overall fuel quality. Previous study reported waste cooking oil with SV higher than 209mgKOH/g able to produce biodiesel upon treated [127, 128].

4.3 Chemical Characterization Of SPO And CPO

The chemical characterization of SPO and CPO in this study were performed by using instrumental analysis to assess the constituent within the chemical.

4.3.1 Functional Group

Evaluating the functional group presented in the SPO and CPO were carried out by using FTIR analysis. The transmittance released from the oils were captured to analyze its wavenumber. Each peak was distinctive to its respective functional group that existed in the oils. As depicted in Figure 4.3, the transmitted wavenumbers for both SPO and CPO were displayed with its respective peaks. The similarities and differences in the peaks between these oils were observed.

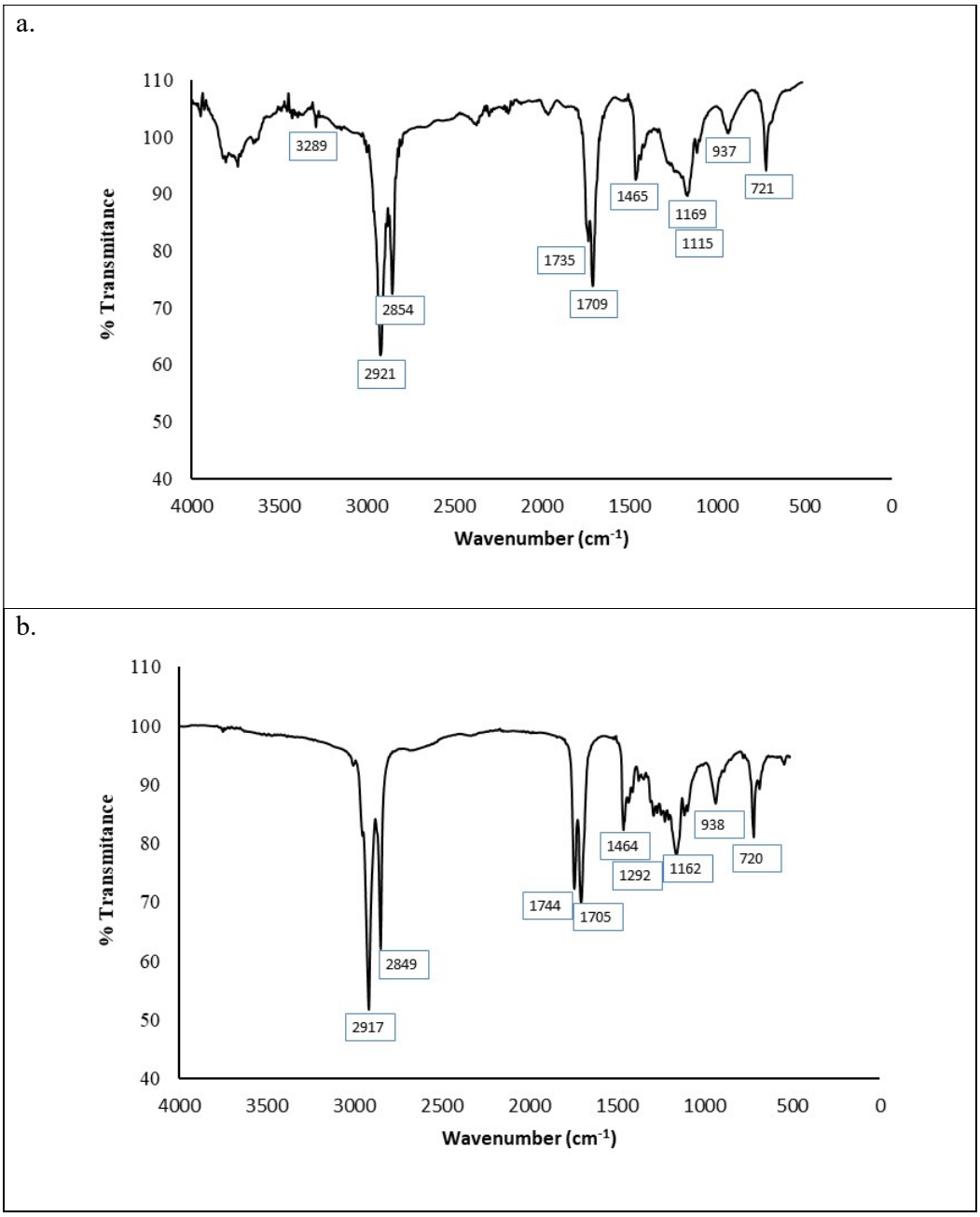


Figure 4.3 FTIR Result Shows Functional Group of a. SPO and b. CPO

The data analyzed was interpreted as shown in Table 4.3. Similar peaks for both oils were identified at 2971 – 2921 cm^{-1}, 2849 – 2854 cm^{-1}, 1734 – 1735 cm^{-1}, 1705 – 1709 cm^{-1}, 1464 – 1465 cm^{-1}, 1162 – 1169 cm^{-1}, 937 – 938cm^{-1}, and 720 – 721cm^{-1}. The identical peaks implied the influence of CH, C=O, O-H and CH_2 band in both oils. [86]. According and to the data analyzed by the FTIR analysis, strong peak was monitored only at 1115 cm^{-1} in SPO but not in CPO. This peak indicates the stretching vibration for both P–O and C–O stretching bands. The presence of phospholipids and

soap in SPO from the palm oil milling process, storage condition, and treatment plant circumstances might be the underlying factor to this finding. There was a similar result from previous research studying the FTIR result in SPO as well [129]. The spectra bands transmitted for CPO in this study were similar to previous research that studied the transesterification of palm oil to biodiesel [130].

Based on the data explored from this analysis, it was proven that both oils exhibit similar functional group characteristics. One of the distinct peaks observed in the FTIR analysis was attributed to impurities from phospholipids and soap present in the SPO, indicating its low quality. High degree of resemblance between these two oils analyzed depicted that SPO conspired of identical chemical feature to CPO. Thus, utilizing SPO as a substitute for CPO in biodiesel production is a logical alternative.

Table 4.3
Functional Groups In SPO and CPO [86, 131, 132].

Wave number (cm^{-1})	Indication	Interpretation	Remarks
3289	O–H stretch	Presence of alcohol group	Appears in SPO only
2917 – 2921	C-H stretching	Presence of CH group / alkene	Appears in both oils. Strong peaks at both oils were observed.
2849 – 2854	C-H stretching	Presence of CH group	Appears in both oils. Strong peaks at both oils were observed.
1735 – 1744	C = O stretching	Presence of carbonyl group / ester	Appears in both oils. Peak was stronger in CPO.
1705 – 1709	C = O stretching	Presence of carbonyl group / ester	Appears in both oils similarly.
1464 – 1465	C-H bending	Presence of C-H group	Appears in both oils similarly.
1162 – 1169	C-O stretching bands	Presence of alcohol	Appears in both oils similarly.
1115	P-O and C-O stretching band	Presence of phospholipids and soap	Appears in SPO only.
937 – 938	O-H band	Presence of carboxylic acid	Appears in both oils similarly.
720 – 721	CH_2 rocking	Presence of C-H group	Appears in both oils similarly.

4.3.2 Fatty Acid Composition

There were pronounce types of fatty acid composition that typically available in the collected SPO and CPO in this study. The fatty acid compositions were then analyzed and summarized in Table 4.4. Types of fatty acids were represented by its carbon chain that comprises of both saturated (carbon chain with no double bond) and unsaturated fatty acid (carbon chain with double bond). From the analysis, it was revealed that palmitic acid emerged as the most abundant fatty acid. The majority of fatty acid presented in both collected SPO and CPO was palmitic acid which comprise of similar composition of 43.38% and 43.90%, respectively. Palmitic acid composed of 16 carbon atom that was a key component discovered in most palm oils. In palm oil, palmitic acid is predominantly extracted from the mesocarp which was the fleshy tissue of the fruit [133]. In addition, the second largest composition was oleic acid with 38.16% for SPO and 39.08% for CPO. High concentration of palmitic acid and oleic acid were expected in CPO as they primarily the fundamental of palm oil.

Table 4.4
Fatty Acid Composition In SPO and CPO

Carbon chain	Fatty acid	SPO composition (%)	CPO composition (%)
C6:0	Caproic acid	0.033	-
C8:0	Caprylic acid	0.078	0.01
C10:0	Capric acid	0.060	-
C12:0	Lauric acid	0.713	0.164
C14:0	Myristic acid	1.223	0.950
C16:0	Palmitic acid	43.337	43.895
C16:1	Palmitoleic acid	0.169	0.245
C18:0	Stearic acid	4.826	3.621
C18:1	Oleic acid	38.160	39.084
C18:2	Linoleic acid	8.814	10.446
C20:0	Arachidic acid	0.327	0.350
C21:0	Heneicosanoic acid	0.585	0.019
C22:0	Behenic acid	0.058	0.060
C23:0	Tricosylic acid	0.110	-
C24:0	Lignoceric acid	0.095	0.073

Other similarities between these two oils were also observed in the fatty acid composition. Ample composition of linoleic acid and stearic acid were detected in both

oils, constituting 8.814 - 10.446% and 3.621 - 4.826%, respectively. On top of that, there were small trace amount of equivalent type of fatty acids in both SPO and CPO. The fatty acid profiles of CPO and SPO were almost identical with respect to myristic acid (0.95-1.2%), palmitoleic acid (0.169 – 0.245%), arachidic acid (0.327 – 0.250%), behenic acid (0.058 – 0.06%), and lignoceric acid (0.073 – 0.095%).

Furthermore, Table 4.5 exhibits the total saturated and unsaturated fatty acids formed that were distinguished based on their presence of double bond. Palmitic acid was the primary saturated acid while oleic acid and linoleic acid are both the dominant monounsaturated and polyunsaturated fatty acid respectively in CPO and SPO. The finding signifies the similarities on the sum of the saturated, monounsaturated and polyunsaturated fatty acids. It was reported that biodiesel with a higher proportion of saturated fatty acids generally has higher cetane number, which indicates better ignition quality [50].

Based on the identified fatty acid components, it was evident that the similarities of major constituents present in both oils implied that SPO has similar feature as CPO. Despite the factor of waste in the trait of SPO, the dominant element of fatty acid exist within the oil is still as identical as CPO. Although SPO has loses its quality and ready to be disposed, it does not compromise the content of fatty acid component within the oil. This phenomenon indicates the ability of reserving SPO to be utilized as source of energy, similar to CPO.

Table 4.5
Total Fatty Acid Compositions In SPO And CPO.

Fatty acids	SPO (%)	CPO (%)
Σ Saturated fatty acids	51.445	49.142
Σ Monounsaturated fatty acids	38.329	39.329
Σ Polyunsaturated fatty acids	8.814	10.446

However, the differences of the fatty acid composition between these oils were also discernible. There is a distinctive amount of fatty acid detected in both oils. The composition of caprylic acid, lauric acid, stearic acid, linoleic acid and heneicosanoic acid were slightly different when comparing between the oils. On top of that, the presence of caproic acid, capric acid, and tricosylic acid were also detected in SPO, but none in CPO. These fatty acids were often found in waste oils [134, 135]. The probable reason to the existence of these foreign fatty acids in SPO is possibly due to the long

exposure between processes and inside the cooling pond in treatment plant. On top of that, impurities originating from the palm oil milling process might also influence the formation of these fatty acids in SPO [69].

In this study particularly, these fatty acids participate in glycerolysis by combining with glycerol, resulting in the formation of glycerides and water. Given that the majority type of fatty acid in SPO was palmitic acid, further experiment of SPO was assumed to be as palmitic acid. In conclusion, it can be deduced that despite being subjected to multiple processing stages from the palm oil mill processes, SPO maintains the integrity of its original fatty acid profile, preserving the same constituent of fatty acids composition. Considering this perspective, SPO is a potential substitute to CPO as biodiesel feedstock.

4.3.3 Chemical Composition

The chemical compound present in both oils were identified by performing GC-MS analysis. The chromatogram peak was showed in Figure 4.4. The compositions of the primary chemical compound present were displayed in Table 4.6 for SPO and CPO. Chemical elements with lower than 1% were not presented in the table because assumed as negligible.

According to the result obtained, palmitic acid was identified at both 17.249- and 15.507-minutes retention time that indicated the presence of palmitic acid with compositions of 18.954% and 24.345% in SPO, respectively. Therefore, the analysis of the collected SPO revealed that palmitic acid constituted a sum of 43.3% of the total fatty acids. This significant proportion indicates that palmitic acid is the predominant fatty acid present in the sample. The dominance of palmitic acid is consistent with typical profiles of palm-derived oils, thereby suggesting that the collected SPO shares similar compositional characteristics with other palm oil fractions including CPO. Palmitic acid is a type of saturated fatty acid with 16-carbon chain.

In addition, SPO was comprised of mixture of chemicals that include fatty acid, alcohol and alkane. It was reported that 10.155% of SPO constituted of oleic acid and 9.418% of the oil content was palmitoleic acid. These chemicals were likely formed from the reactions of palm oil milling processes and impurities from the waste plant. There was not yet report published by scholar on the chemical composition of SPO. The dominant composition detected in the CPO also composes of high of palmitic acid that

conspired of a total of 36.675%. The other dominant composition was oleic acid at 4.885%. The abundance of fatty acids in the CPO was anticipated, following the minimum impurities exist in the oil.

Table 4.6
Primary Chemical Composition In SPO And CPO.

Retention Time, minutes	Molecular formula	Compound	Composition (%)
SPO			
17.249	$C_{16}H_{30}O_2$	Palmitic acid	24.345
15.507	$C_{16}H_{32}O_2$	Palmitic acid	18.954
37.695	$C_{18}H_{34}O_2$	Oleic acid	10.155
39.188	$C_{16}H_{30}O_2$	Palmitoleic acid	9.418
18.482	$C_{19}H_{38}O_4$	Palmitoyl glycerol	2.086
16.116	$C_{19}H_{40}O_2Si$	Trimethylsilyl hexadecanoate	2.357
21.050	$C_{18}H_{32}O$	Linolenyl alcohol	1.960
CPO			
15.800	$C_{11}H_{22}O_2$	Palmitic acid	21.684
17.543	$C_{11}H_{22}O_2$	Palmitic acid	13.431
17.822	$C_{18}H_{34}O_2$	Oleic Acid	4.885
16.292	$C_{16}H_{30}O_2$	Palmitic acid	1.56

Following the analysis on both oils, it can be deduced that there were apparent differences in terms of the chemicals existed in both oils. It should be highlighted that SPO was an unstable oil with mixture of numbers of components. It was observed that SPO has many impurities and other foreign materials due to its waste attributes, compared to CPO. However, it is also essential to emphasize that fatty acid is still maintained as the predominant constituent in SPO. Therefore, this contributes to the key factor of implementing SPO as the potential biodiesel feedstock and also the requirement of treatment step for SPO prior to producing biodiesel. Furthermore, it is important to acknowledge that fatty acid composition analysis differs from chemical composition analysis. Fatty acid composition analysis focuses on quantifying individual fatty acids such as palmitic, oleic, linoleic, and stearic acids in palm oil. Chemical composition encompasses a broader set of constituents in palm oil, including triacylglycerols, free fatty acids, minor bioactive components such as tocopherols and carotenoids, and various lipids beyond just fatty acid chains. Therefore, it is relevant to

obtain results showing that the chemical composition does not necessarily correspond directly with the fatty acid composition. Hence, differences between chemical composition and fatty acid composition were scientifically justifiable.

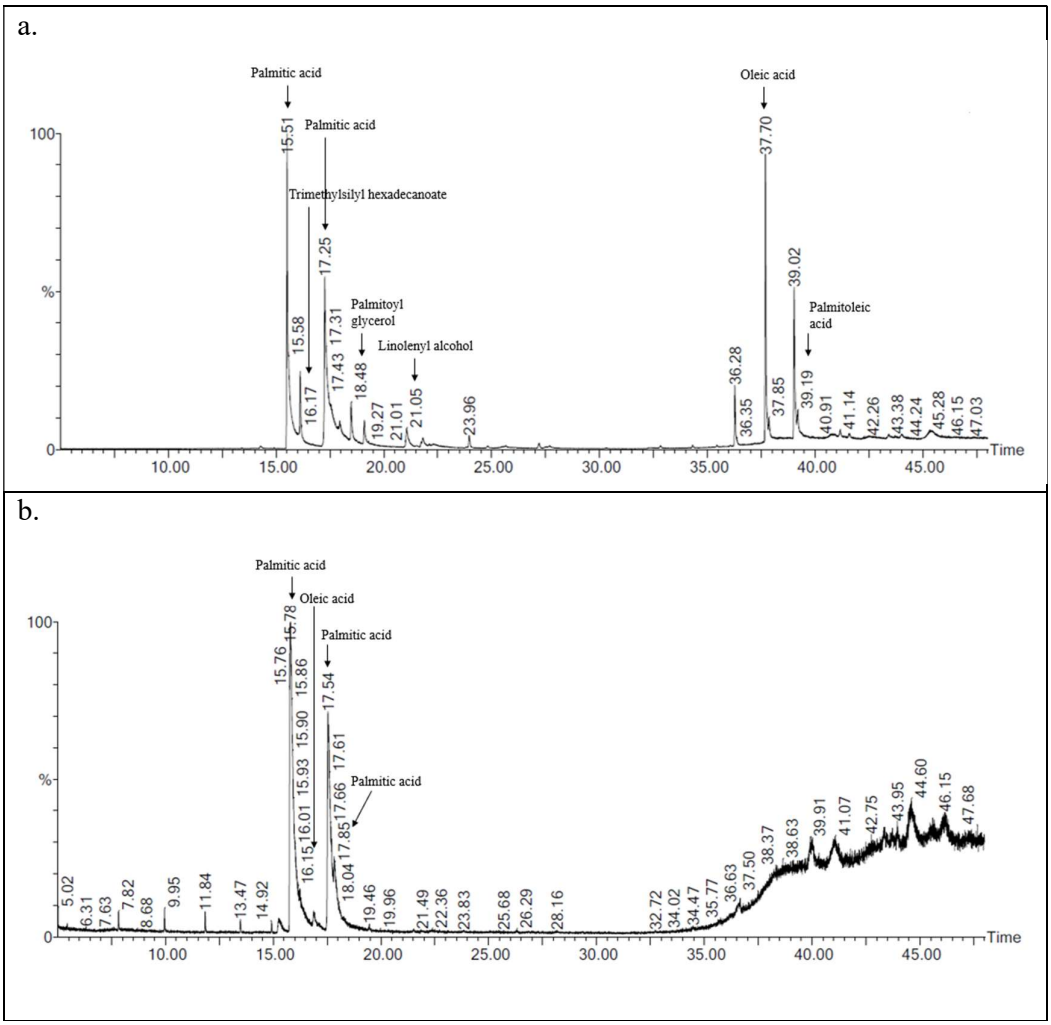


Figure 4.4 Chromatogram Peaks For a. SPO And b. CPO

4.4 Summary Of Characterization Of SPO And CPO

In instance, upon evaluating both physical and chemical characterizations of SPO and CPO, there were distinctive similarities and differences discovered in various perspective. To summarize, SPO was a low-quality oil with excess value of free fatty acid, moisture content and saponification value. Those values were relatively higher than the standard oil used as biodiesel raw material, makes it recalcitrant to be regarded directly as biodiesel feedstock.

However, the potential and prospective of SPO should be highlighted because it comprehends similar features in most of chemical perspective. Functional groups and, fatty acid compositions indicate the similarities of both SPO and CPO. Chemical composition for both oils was different due to numbers of foreign materials in SPO. Pre-treatment of SPO was conceptual to refine the oil by reducing the free fatty acid content to be applied as potential biodiesel feedstock. Therefore, SPO should be explored further on its potency to convert into biodiesel by applying the constructed methods and strategies.

4.5 Pre-treatment Of SPO Using Glycerolysis

The process of glycerolysis was conducted with the aim of reducing the value of FFA in SPO. The initial value of FFA which was 59%, was experimented repeatedly in different parameters with distinctive range. The procedure was set for 3 hours long with constant speed of 300rpm. Different parameters affect the reduction of FFA differently, in terms of its rapidity and efficiency.

4.5.1 Effect Of Temperature

Temperature influences dominant value to the efficiency of glycerolysis. For this study, the final FFA at 3rd hour for every parameter was depicted as in Figure 4.5. The initial FFA was as reported previously which was 59%. From overall observation, it can be seen that the final result of FFA value at 170°C, 190°C and 220°C ranging from 4.9% to 0.42%. Temperature at 220°C with every related parameter reflected lowest values of final FFA from the glycerolysis reaction, falling within the range of 1.8% to 0.42%. These values of FFA content in the SPO were significant as it comprised within the allowable FFA content for biodiesel feedstock. It was evident that higher temperature gives better results in terms of FFA reduction. Similarly to previous study by Mićić et al., the highest FFA reduction (79%) achieved at 220°C in 120 minutes, while only 42% of FFA reduction achieved at 170°C in longer duration which was 180 minutes [112]. The pertinent of high temperature to the effect of glycerolysis is due to the elevated kinetic energy that promotes the solubility of glycerol within the oil. On top of that, the interactions between reactants molecules with the active sites on the catalyst surface increases at higher temperature that boosts the reaction efficiency

[136]. Therefore, for this research, it was established that the best condition for glycerolysis in reducing the FFA in the SPO was at 220°C.

According to Selemani and Kombe, glycerolysis is typically accomplishes at high temperature [9]. However, the range would be different depending on the original value of FFA and the targeting final value of FFA. As example, to reduce the presence of FFA from 6.15% to 0.28% in crude palm oil, a lower range of temperature at 55 to 85°C within 90 minutes is feasible [89]. The reported previous study deduced that glycerolysis was able to execute at lower range of temperature with 95% of FFA reduction in the case of oil with relatively lower value of FFA. On the other hand, for elevated initial FFA value that usually occur at low quality of oil like SPO or waste cooking oil, it was rather challenging and in need of higher temperature. The common range of temperature that is adequate and significant in lowering the FFA at high initial value was at 170 to 220°C [51, 83].

According to Figure 4.5, at 170°C, the lowest FFA value obtained was 3% at maximum glycerol amount (1:2 SPO to glycerol mol ratio) and catalyst loading (1.0wt%). The FFA content achieved at the final hour was the bare minimum for the allowable value for biodiesel production with elevated amount of glycerol and catalyst required. On the other hand, the value of FFA at this temperature with other sets of parameters were ranging from 4.9% to 3.5%. These values were ineffectual and non-ideal for biodiesel production. The justified explanation for these outcomes at this temperature was mainly due to the inadequate time to achieve the desired value of FFA. Similar result can be observed from study conducted by Miyuranga et al. when waste cooking oil with 19% FFA reduced to only 4% FFA within 2 hours by running glycerolysis at 180°C with 1wt% KOH catalyst and 1:4 oil to glycerol ratio [84]. In this study, 59% of initial FFA of SPO was believed as one of the highest values of FFA for waste oils that is taken to produce biodiesel. It can be concluded that at this temperature (170°C), higher duration (more than 3 hours) with higher amount of glycerol and catalyst loading is needed to achieve the desirable result that is lower than 3% of FFA.

Since the FFA was checked for every hour throughout the gycerolysis process, overall analysis of the hourly FFA reduction result for every parameter was depicted in Figure 4.9 to 4.11, according to its temperature. Drastic depletion of FFA from 59% to 7.96% was monitored at first hour at 170°C with 1:1 oil to glycerol ratio and catalyst at 1.0wt% as shown in Figure 4.9. The introduction of high temperature at the early stage

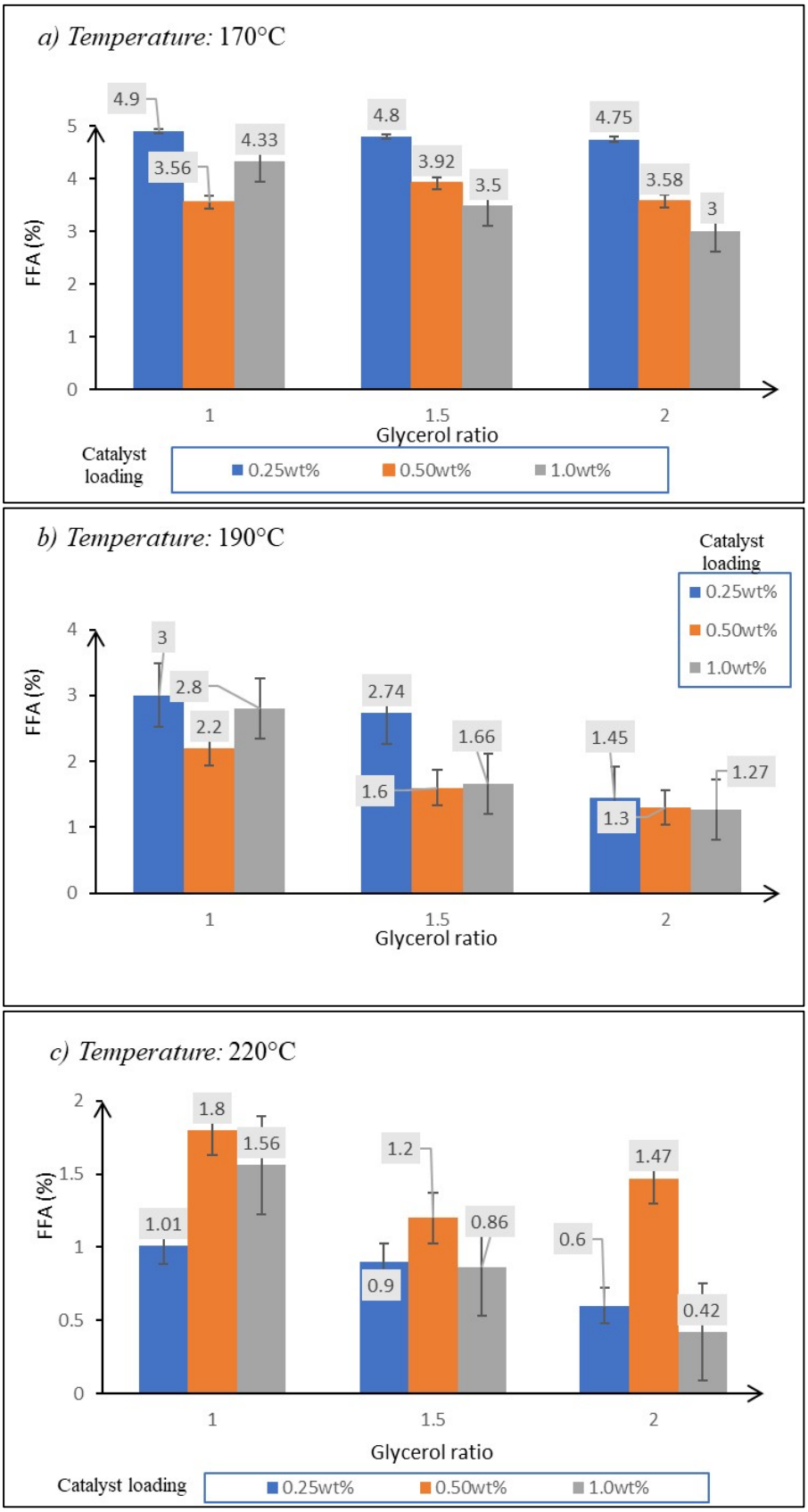


Figure 4.5 Final FFA Values For a) At 170°C, b) At 190°C And c) 220°C.

of the reaction has impactfully lower down the viscosity of the oil that simultaneously promotes particles mobility and hence, improve the FFA conversion. [137]. As supported by previous studies, extreme declination of FFA content was observed at early hours when the reaction was heated at high temperature [51, 85, 89].

On the contrary, the result exhibited impressive finding when applying glycerolysis at 190°C and 220°C. Higher reaction temperature increasing the rate of reaction and conversion, supported by the increasing number of energy collision [137]. This trend can be corroborated due to the complexion of endothermic of esterification reaction [137]. Based on Figure 4.5(b) and (c), all conditions achieved the allowable amount of FFA for biodiesel feedstock. The lowest FFA (0.42%) that was 99% FFA reduction efficiency was acquired at the maximum condition (220°C, 1:2 SPO to glycerol mol ratio and 1.0wt% of catalyst). Previous study reported that the most efficient temperature for glycerolysis to reduce the FFA and form glycerides in palm fatty acid distillate is at 220°C, as higher than that may burn the oil and effect the efficacy. Furthermore, it was reported that at this temperature, reduction of FFA by glycerolysis can be achieved faster [138]. However, if energy conservation and cost efficiency take precedence in the analysis factor, 190°C was already sufficient and satisfactory for the oil pre-treatment prior to produce biodiesel. This verdict was deduced because at 190°C, the final FFA content was ranging from 3% to 1.27%, which was adequate as the standard for biodiesel feedstock.

Figures 4.7 and 4.8 illustrated the progressive decrease in FFA concentration with respect to time (hourly intervals) at 190°C and 220°C, respectively. Drastic declination of FFA was observed at most of the results at first hour at both temperatures. This trend implies that elevated temperature significantly contributes to the formation of glyceride, regardless little amount of glycerol and catalyst are supplied in the reaction. The spike reduction of the FFA values in the first 60 minutes implied elevated rate of reaction occur at the early phase of the reaction. The second phase was observed at the second hour when the rate of reaction moderately dropped as the declination of FFA is slightly gradual. At the third hour, the majority of the results were constant as the reaction has reaching its equilibrium stage. The analysis was relatable as study conducted by Roslan et al. [17]. The nature of glycerol that was hydrophilic steered the reactant to become less soluble in organic solution and hence affecting the homogeneity within the reaction. Higher temperature assists in providing better miscibility and

mobility for the reactants while dropping the reaction viscosity that consequently increases the rate of reaction and accelerates FFA conversion significantly [83]. This deduction can also be supported by Arrhenius equation that stated rate of reaction escalates exponentially with temperature due to the frequency of collision between molecules within the reactions.

Hence, it can be concluded that conducting glycerolysis reaction at 170°C has been shown to be ineffective for this reaction, On the contrary, both 190°C and 220°C had a substantial positive impact on the reaction performance indicating their optimum for the reaction. However, in selecting the most ideal temperature for this method, many key factors need to take into consideration including energy conservation, safety reason and cost-effective. Therefore, 190°C was a justifiable choice as the optimal temperature based on the observed outcomes, as the final FFA achieved in the treated SPO were lower than the 3%, that is required to be feasible as biodiesel feedstock. However, the best achieved result obtaining the lowest FFA content of 0.42% from 59% was at 220°C.

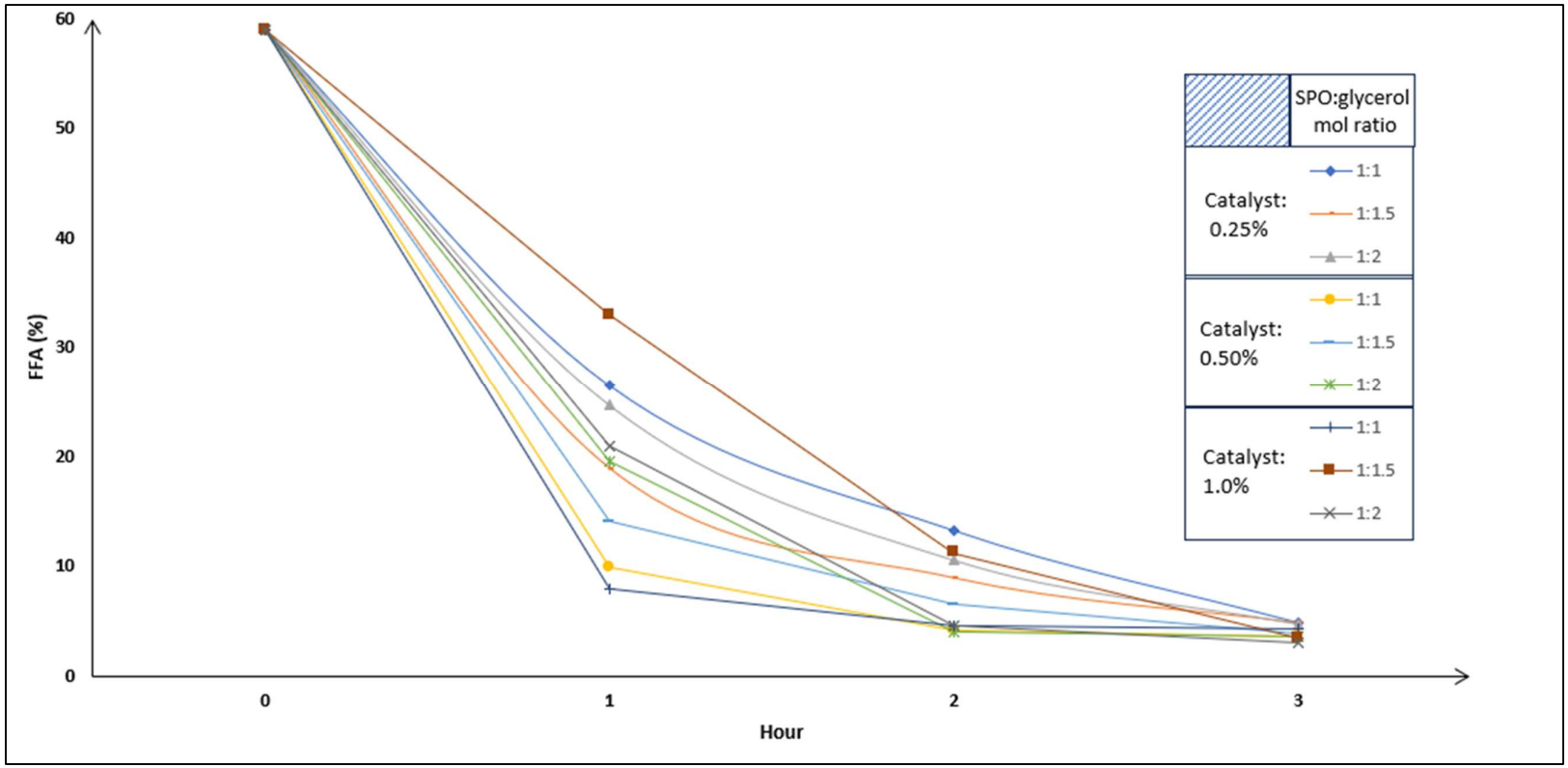


Figure 4.6 FFA Result Hourly At 170°C With Different Parameter.

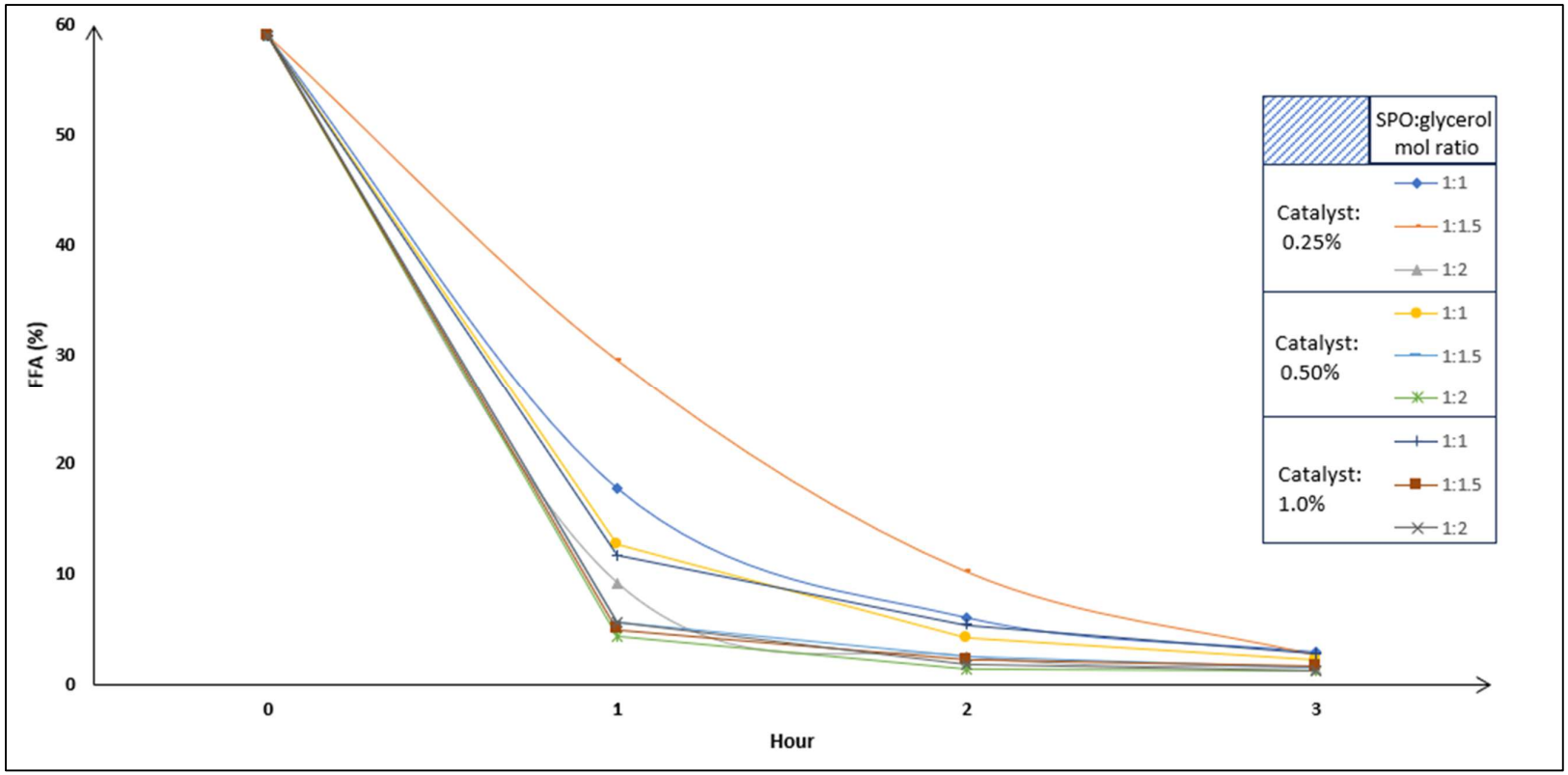


Figure 4.7 FFA Result Hourly At 190°C With Different Parameter.

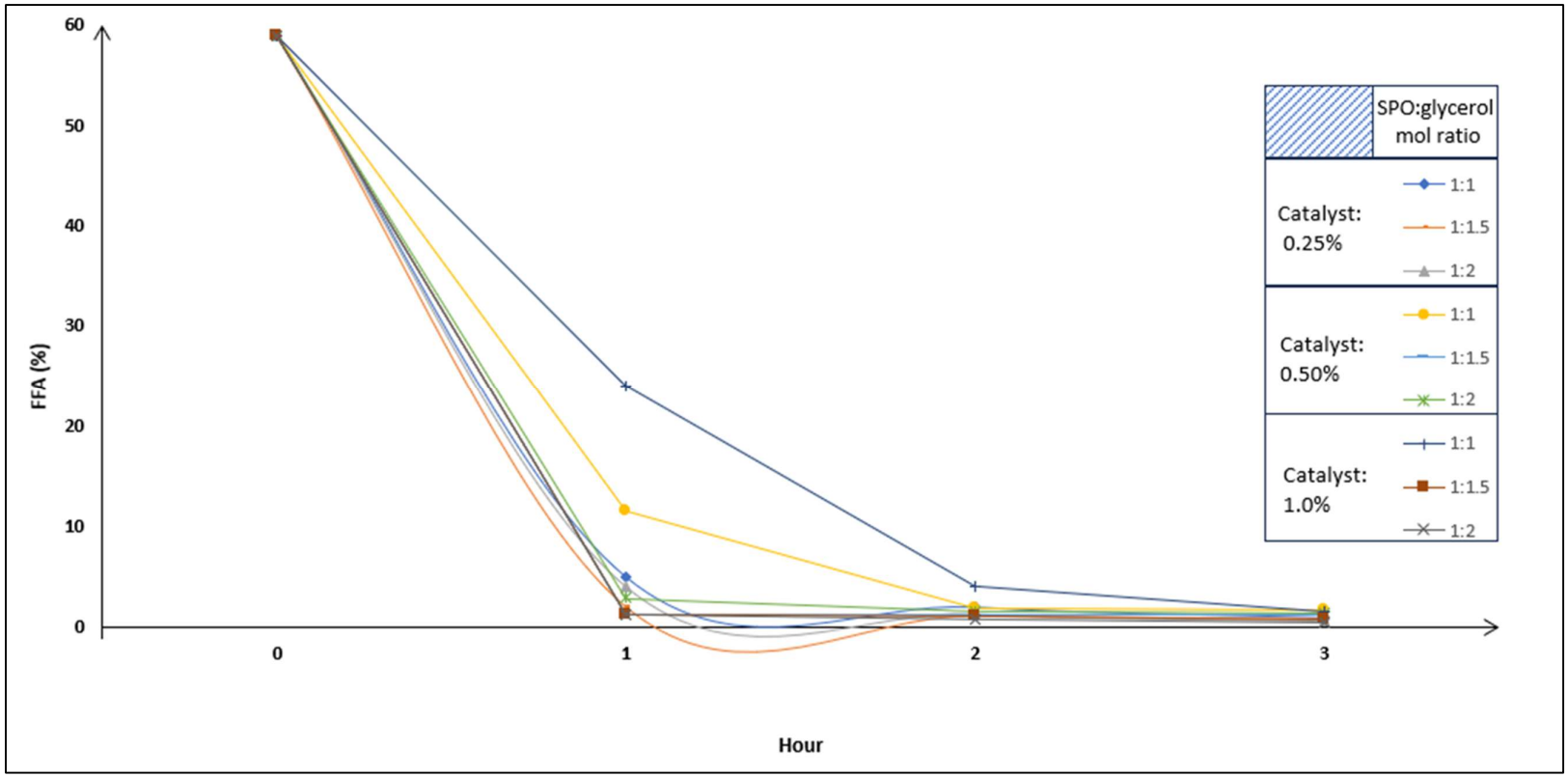


Figure 4.8 FFA Result Hourly At 220°C With Different Parameter.

4.5.2 Effect Of Catalyst Loading

The incorporation of ZnO as catalyst in the glycerolysis process to assist in the rate of reaction provides significant impact to the reduction of FFA in order to treat SPO. ZnO was chosen as the applied catalyst to investigate the efficacy ot metal oxides on the glycerolysis reaction. Previous scholar has established ZnO as an efficient catalyst in esterification of fatty acid with long chain alcohols or polyols like glycerol [13]. Wang et al. summarized the proficiency of ZnO-containing catalyst in facilitating the reactions involved in biodiesel production [139]. It was vital to identify the optimum catalyst loading required to lower down the FFA. It was also important to analyze the degree of implications of catalyst addition to the rate and efficiency of the reaction.

In this study particularly, three different amounts of catalyst were tested towards the reaction to discover the ideal condition. Referring to Figure 4.9, final value of FFA for each parameter in different catalyst loading were displayed accordingly. It was detected that upon applying ZnO at 0.25wt%, the range of the final FFA were at 4.9% to as low as 0.6%. The obtained result implied that the minimum amount of catalyst was able to reduce FFA to the desired amount which is less than 3%. The condition at 0.25wt% ZnO and 220°C at both 1:1.5 and 1:2 SPO to glycerol ratio gave outstanding results which were 0.9% and 0.6% of FFA, respectively. The conversion of FFA for both conditions were approximately 99% that signifies optimum loading of catalysts were applied. Recent research has studied the effect of zinc glycerolate as catalyst to the glycerolysis of acidifed palm oil, gutter oil and acidified soybean oil. 6.45mmol or approximate 0.3wt% of zinc glycelorate succeeded to reduce down more than 90% of acid value in all respective oil in 4 hours reaction time [12]. The mechanism of ZnO as catalyst initiated with the extraction of proton from glycerol before converting them into a free radical. The formation of glycerides stimulates when the free radical attacks the existed FFA. Raising the amount of catalyst loading to the reaction enhances the production of glyceroxide radicals that ultimately reducing the FFA by converting them into glycerides [86].

However, increasing ZnO to 0.5wt% in this study does not improve the FFA reduction necessarily. As observed in the result, final FFA at this condition was within the range of 3.56% to 1.47% of FFA. The lowest value acquired was not as par when compared to at 0.25wt% loading. The underlying factor to this outcome may possibly

due to the formation of undesired reaction products as similarly suggested by previous report [140]. Additionally, excessive amount of ZnO in glycerolysis may elevate the viscosity of the mixture and hindering the reaction [84]. High viscosity of SPO may be one of the key elements to this consequence. On top of that, the presence of many components including foreign material in SPO as analyzed before may also be one of the probable reasons for this outcome. The proper balance of catalyst loading and other parameters were essential to ensure the reaction is optimized. It was observed that raising catalyst loading at 0.5wt% was insignificant as the result was not satisfactory at the final hour. As reported by Nindya et al., increasing the loading of catalyst will increase the contact between reactants and their respective active sites. However, crossing certain maximum limit will not give a significant impact to the reaction system [141].

The value of 0.42% of final FFA were monitored upon applying the maximum condition of glycerol, catalyst and temperature. ZnO at 1.0wt% was able to transform high content of FFA into glycerides by forming multiple glyceroxide radicals [142]. The synthesis of the different parameters also plays vital roles towards the primary reaction of glycerolysis. The correlation between the distinctive conditions were necessary because one condition complement the other. Recent study employed response surface methodology to analyze the optimum condition for glycerolysis and discovered 75.17°C, 235.06 rpm, 3.57:1 glycerol to FFA molar ratio, and 0.98 wt.% KOH catalyst were able to reduce FFA content from 6.9% to 0.24% FFA in CPO. They suggested that temperature, catalyst loading, glycerol amount, and stirring rate corresponded to each other that contribute to the final FFA result [142].

Based on Figure 4.8, SPO were observed to reduce its FFA content drastically from 59% to 1.35% at the first hour at catalyst 1.0wt%, 220°C and 1:1.5 oil to glycerol ratio. The presence of maximum catalyst loading contributes to the substantial change at this condition at the early phase of glycerolysis. Study by Tu et al. required extended reaction time, which was at 210 minutes at 215°C to reduce FFA content from 29% to 2.9% in grease trap waste without the presence of catalyst which implied the importance of catalyst to the speed of the reaction [85]. The application of ZnO was vital in order to speed up the esterification reaction. ZnO was regarded as heterogenous catalyst, that was one of the established catalysts employed for glycerolysis reaction. However, there were limited study on the application of metal oxides, especially Zn, in previous study

reported [20]. Therefore, this study was one of the early studies on investigating the efficacy of ZnO in glycerolysis reaction.

The selection of catalyst loading was crucial in order to ensure the efficacy of the reaction. For this study particularly, although the best result which was the lowest FFA content acquired is at catalyst loading 1wt% at all temperature, selecting catalyst loading at 0.25% as the ideal condition was already sufficient. This selection was reasonable because when applying catalyst at 0.25wt%, FFA can successfully reduce to as low as 0.6%. The treated SPO at that value was already adequate to make as biodiesel feedstock. On top of that, the selection was convenient when considering the economical and sustainable point of view. However, the best result that accomplished the lowest result of FFA was at ZnO loading of 1wt%.

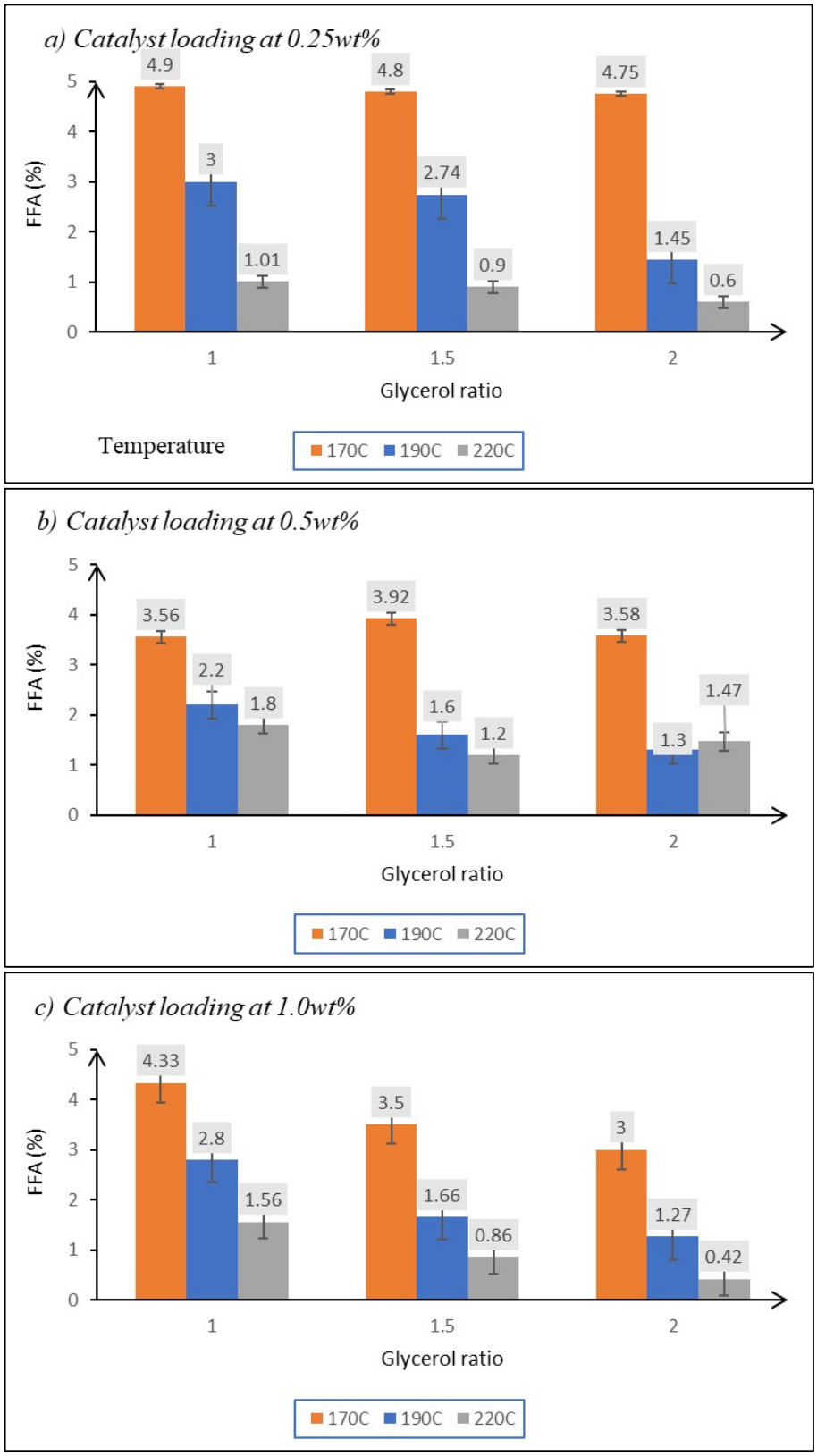


Figure 4.9 Final FFA Values For Catalyst Loading a) at 0.25wt% b) at 0.5wt% and c) 1.0wt%

4.5.3 Effect Of SPO To Glycerol Mol Ratio

In this study, the amount of glycerol added to the reaction were distinctive to analyze the implications of different mol ratios of SPO to glycerol. The amount of glycerol supplied to the reaction act as one of the key players to the rate of reaction in glycerolysis to reduce the FFA within oil. Excess amount of glycerol was believed to enhance the reaction by allowing the reaction to always shift to the right and simultaneously prevent the reaction to be shifted to the left [6]. This application was supported by the consequence of Le Chatelier's Principle.

According to Figure 4.11, from the overall observance, it was found that glycerolysis reaction at all three mol ratio offered profound results. Although at the low ratio of 1:1 SPO to glycerol mol ratio implying there was no excess of glycerol, the targeted FFA reduction were achievable at 190°C and signifyingly great at 220°C. The result obtained were ranging from 3% to 2.2% and 1.8 to 1.01% of FFA, respectively. These reduced content of FFA were adequate to produce biodiesel. The clarification to this result was presumably due to the elevated kinetic energy in the oil molecule at high temperature boosts the formation of glycerides although there was limited quantity of glycerol. On top of that, given that the 1:1 mol ratio was 1 mol of glycerol reacts with 3 mol of FFA that favour the production of triglyceride, applying this ratio may reduce FFA significantly but not necessarily enhance the formation of triglyceride. Monoglyceride and diglyceride may form abundantly while able to reduce the FFA content. However, mol ratio of 1:1 was not able to reduce FFA significantly at 170°C. The low temperature could not synthesize with no excess of glycerol to perform glycerolysis significantly. This finding implied that the synergy at this condition (170°C and 1:1 SPO to glycerol mol ratio) was not as efficient compared to that of higher values.

When performing glycerolysis of SPO at of 1:1.5 mol ratio and temperature at 220°C, applying catalyst loading of 0.5wt% give slightly higher FFA value compared to that at catalyst loading of 0.25wt%. The possible reason for this outcome was because of the probability of excess glycerol that may interrupt the catalysis performance by covering the catalyst surface. Hence, affecting the reaction performance [19]. However, improvement of the result were observed when high glycerol ratio were introduced. When performing the reaction at ratio of 1:2 of SPO to glycerol, the reduced FFA were substantially outstanding compared to others with the range of 91.9% to 99% FFA

conversion. This condition was presumed to be effectual due to the abundant amount of glycerol supplied have reacted with almost every content of FFA in the SPO to form glycerides. The stated occurrence was illustrated as in Figure 4.10 for better understanding. When the excess amount of glycerol attached to 3 mols of free fatty acids, triglyceride which was the major constituent to produce biodiesel was formed. On the other hand, some of the glycerol would be attached only to 2 or 1 mols of fatty acids, that resulting in formation of diglyceride and monoglyceride, respectively. Ultimately, when these free fatty acids reacting with the vast amount of glycerol, the elevated FFA content in the SPO was reduced significantly, and transforming to these glycerides. It was reported that the maximum ratio to ensure the optimization of glycerolysis is at 1:6 oil to glycerol. Beyond than this value will not benefit the reaction, but only adding glycerol at the end product [142].

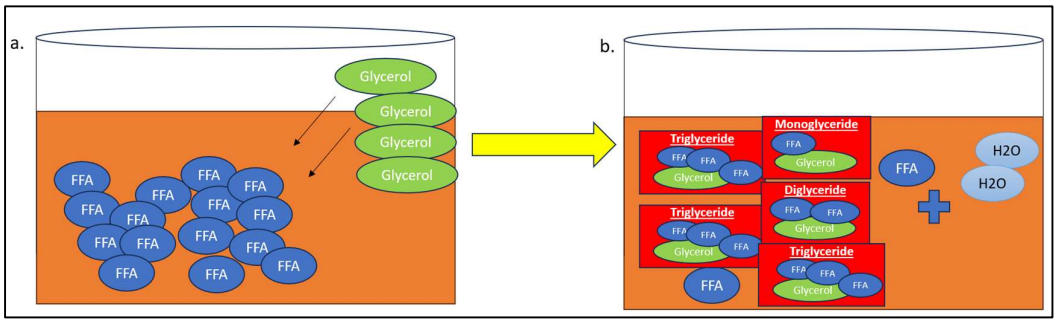


Figure 4.10 a) Excess Of Glycerol Supplied To The Abundance Of FFA Content In SPO And b) Formation Of Glycerides And Water

However, elevated amount of pure glycerol was not advisable because they may interfere with the homogeneity of the reaction and subsequently impact the mass transfer efficacy [86]. Crude glycerol that is commonly collected from by-product of biodiesel can be applied as alternative for pure glycerol. Recent study reduced FFA in brown grease to lower than 1% by applying crude glycerol at 1:1 mol ratio and 230 °C for 150 min. They deduced that this application can contribute to a closed-loop process in biodiesel production and promote the reusability of crude glycerin without energy-intensive purification [85].

In conclusion, for this particular study, excess glycerol was required when lower temperature was applied in the glycerolysis. Conversely, upon applying the reaction at higher temperature (190°C-220°C), mol ratio of SPO to glycerol ratio 1:1 that favors triglyceride is adequate to achieve the targeted FFA conversion in SPO. However, since the dynamic between all these parameters were crucial in the reaction efficiency, the

most ideal SPO to glycerol mol ratio was at 1:1.5. This condition was preferred as it resulted in an acceptable FFA value while considering the influence of other variables (190C, 0.25wt% catalyst loading and SPO to glycerol ratio 1:1.5). The best result achieving the lowest FFA at 0.42% was at SPO to glycerol mol ratio of 1:2 which was the maximum amount of glycerol in this particular study.

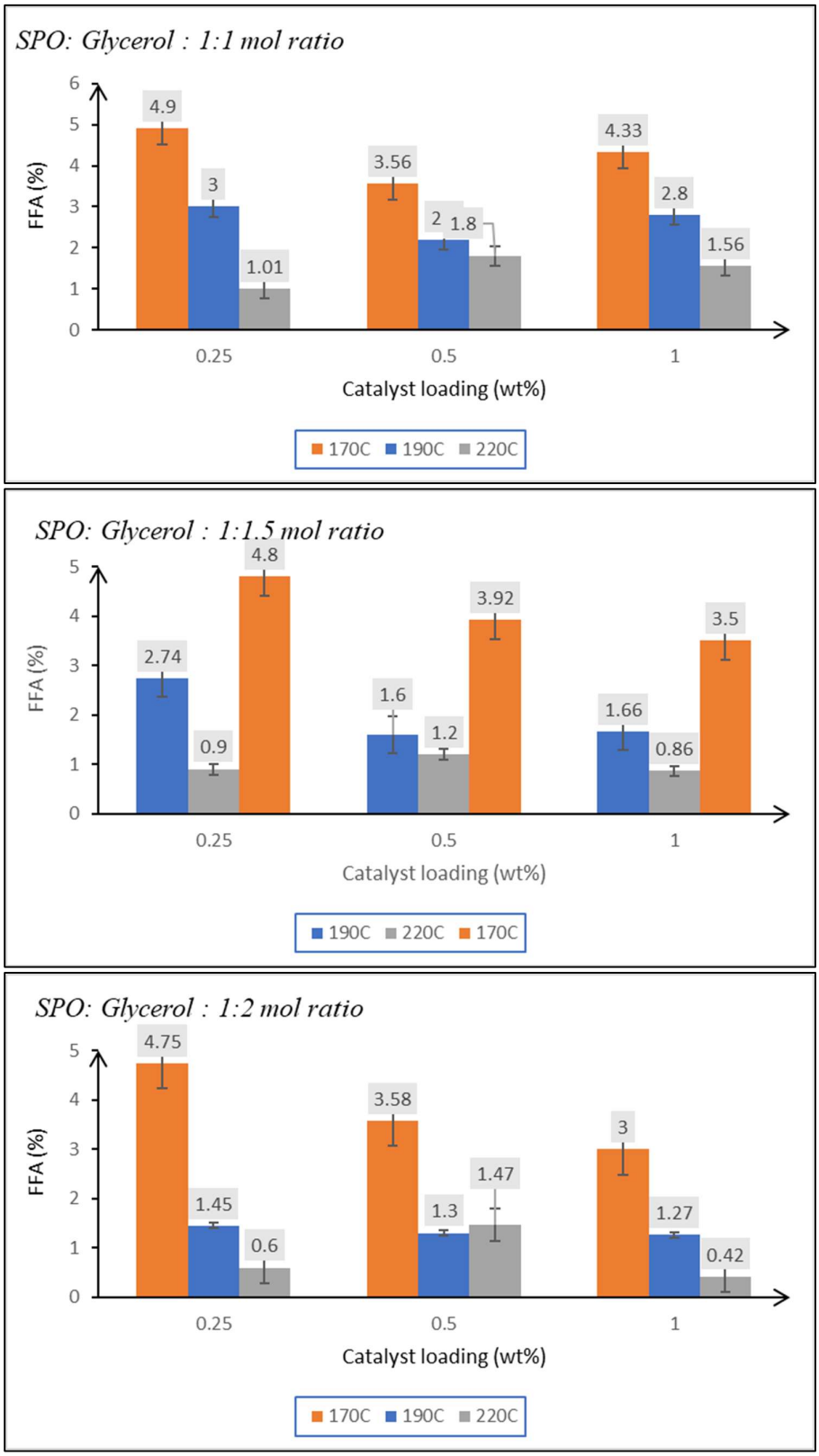


Figure 4.11 Final FFA Values For ratio a) at 1:1 b) at 1:1.5 and c) 1:2

4.6 Summary On Esterification By Glycerolysis

In this study, significant reduction of FFA content were achieved. The final FFA achieved by SPO after glycerolysis process at every operating condition was displayed at Table 4.7. Initial FFA content in SPO of 59% was successfully reduced in all condition, with the lowest FFA content attained being 0.42% indicating 99.4% FFA reduction. This result was achieved at temperature of 220°C, ZnO catalyst loading of 1.0wt% and 1:2 of SPO to glycerol mol ratio.

The final FFA at all condition at 190°C and 220°C have achieved the minimum allowable content of FFA to produce biodiesel. It can be confirmed by the FFA value obtained at the end of reaction which were lower than 3% with a range of 94.9 to 99.3% FFA reduction. On the other hand, applying glycerolysis at temperature 170°C were not be able to reach the allowable standard at every incorporated parameter. However, temperature at 170°C was capable to achieve 91% - 94% FFA conversion which should be highlighted significantly. Similar previous study reported that CPO with 6% of FFA content was successfully reduced by glycerolysis at 95.45% applying 0.75wt% catalyst loading and 1:4 oil to glycerol mol ratio but at lower temperature of 80°C [48]. Other report also mentioned of 90% FFA reduction of vegetable oil at 160°C and 5wt% catalyst loading was successfully achieved by glycerolysis method [143].

The ideal conditions for this study were at 190°C, 0.25wt% catalyst loading and 1:1.5 SPO to glycerol mol ratio. The primary factor to the selection of these parameters were due to the ability to lower down the 59% of FFA to 2.74%. These parameters were adequate and significant to perform glycerolysis efficiently and achieved the standard value of FFA in order to produce biodiesel. Furthermore, although at elevated temperature, catalyst loading and excess glycerol offered enhanced performance, the mentioned parameters were satisfactory for operating efficiency, cost-effective and promoting energy-conservation. The objective for this study was achieved.

Table 4.7
Final FFA Value And FFA Reduction For Every Operating Parameter.

Test	Temperature (°C)	Catalyst loading (%)	SPO to glycerol mol ratio	Initial FFA (%)	Final FFA after 3 hours (%)	FFA reduction (%)
1	170	0.25	1:1	59	4.9	91.7
2	170	0.25	1:1.5	59	4.8	91.7
3	170	0.25	1:2	59	4.75	91.7
4	170	0.5	1:1	59	3.56	94.0
5	170	0.5	1:1.5	59	3.92	93.4
6	170	0.5	1:2	59	3.58	93.9
7	170	1.0	1:1	59	4.33	92.7
8	170	1.0	1:1.5	59	3.5	94.1
9	170	1.0	1:2	59	3.0	94.9
10	190	0.25	1:1	59	3.0	94.9
11	190	0.25	1:1.5	59	2.74	95.4
12	190	0.25	1:2	59	1.45	97.5
13	190	0.5	1:1	59	2.2	96.3
14	190	0.5	1:1.5	59	1.6	97.3
15	190	0.5	1:2	59	1.3	97.8
16	190	1.0	1:1	59	2.8	95.0
17	190	1.0	1:1.5	59	1.66	97.2
18	190	1.0	1:2	59	1.27	97.8
19	220	0.25	1:1	59	1.01	98.3
20	220	0.25	1:1.5	59	0.9	98.5
21	220	0.25	1:2	59	0.6	98.9
22	220	0.5	1:1	59	1.8	97.0
23	220	0.5	1:1.5	59	1.2	97.8
24	220	0.5	1:2	59	1.47	97.6
25	220	1.0	1:1	59	1.56	97.4
26	220	1.0	1:1.5	59	0.86	98.5
27	220	1.0	1:2	59	0.42	99.3

4.7 Biodiesel Production By Transesterification

After performing glycerolysis to SPO, the FFA content in SPO were reduced. According to the result acquired from the reduction reaction, the lowest FFA achieved in the SPO was 0.42%. This value was the lowest and the best result accomplished for

the reduction of FFA in this study. The treated SPO with 0.42% of FFA was then reserved for further process that was the production of biodiesel. This procedure was the evident technique to authenticate the feasibility of SPO to convert into biodiesel. Since it was proven for the accomplishment to reduce FFA from 59% to 0.42% with 99.4% reduction efficiency, the next rationale application was to verify its potential to produce biodiesel. Transesterification process was then carried out by applying ethanol and KOH as reactant and catalyst, respectively to produce biodiesel.

After maintaining the reaction for 3 hours in a constant temperature of 70°C and 300rpm stirring rate, the synthesized product was allowed to cool down to room temperature. Figure 4.12 depicts the cooled product after transferring into a separating funnel for separation process for 24 hours. It was observed that the denser sediment was deposited at the bottom. The sediments were removed to separate them from the upper part of the mixture which was the final product. These sediments were assumed to comprise of other impurities including excess ethanol, catalyst and glycerol [50]. Other researchers extract the recovered glycerol by washing with hexane for reusable purposes [144]. The upper part of the separation was collected as the produced biodiesel from the reaction. This result was similar to previous report [40].

Figure 4.13 displayed the recovered biodiesel after the sediments were removed. From the observation, the biodiesel produced was in light brown colour and in liquid form in room temperature with no presence of soap formation. Previous study reported similar physical attribute of biodiesel from waste cooking oil [145]. On top of that, it was observed that there was no detection of soap formation in the final biodiesel product. High FFA in waste oils including SPO influences to the soap formation of the biodiesel product and consequently impacted the yield of the biodiesel. Relying from the physical observation alone, this outcome implied the importance of reducing the FFA in the feedstock as the pre-treatment process to avoid the formation of soap when producing biodiesel from SPO. Furthermore, the condition produced also indicated the high FFA in SPO was successfully reduced to the allowable amount to produce biodiesel efficiently as also suggested by previous scholar [60].

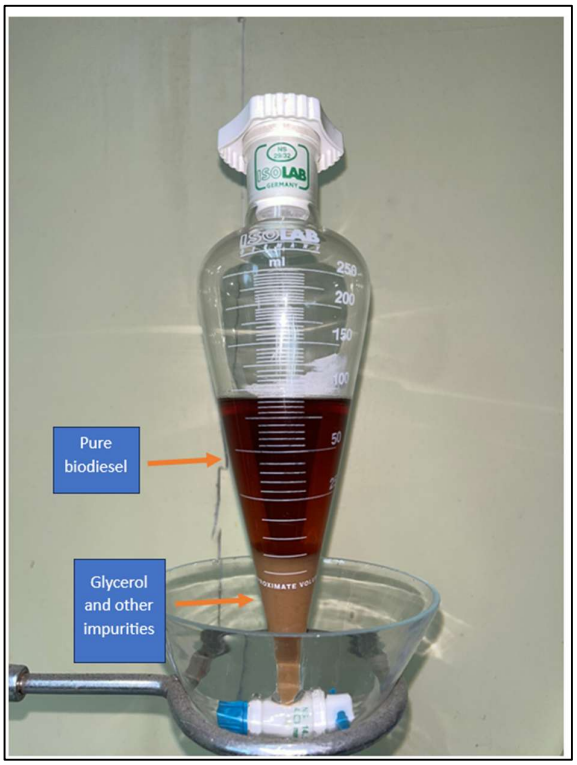


Figure 4.12 Produced Biodiesel Transferred Into Separating Funnel For Separation Process

Figure 4.13 Biodiesel Collected

4.7.1 Analysis Of Biodiesel Produced By FTIR

In order to verify the success of the transesterification reaction and biodiesel was produced from the treated SPO, FTIR was employed as an analysis tool to detect the presence of FAEE in the product. Figure 4.14 depicts the FTIR spectra bands on the

biodiesel produced from this study. The identification of each absorbance peaks was then distinguished as in Table 4.8.

The presence of absorbance peaks detected at 3802 and 3740cm^{-1} were corresponded to the presence of O-H bonds from the O-H group. The absorbances most likely to appear due to the presence of excess ethanol and glycerol that is the by-product. According to study by Jin and Li, present of metal oxide may resulting to these apparent peaks [146]. The excess of ZnO from the glycerolysis reaction may be the factor to this outcome. On the other hand, sharp peaks at 2921 and 2854cm^{-1} were observed from the biodiesel spectrum, and interpreted as the presence and formation of C-H group. According to Shalaby and El-Gendy, the peaks transmitted associated with the formation of CH_2 and CH_3 in biodiesel. [147]. On top of that, the presence of fatty acid such as palmitic acid may contribute to this appearance.

The primary functional groups that typically observed to the indication of FAEE components are from the uptake of C = O and C-O groups. These group relates to the presence of esters. [148]. According to Rabelo et al., peaks observed at the region between 1800-1700 cm^{-1} were typically associated with the stretching of C=O that were common in esters [149]. The peak observed at 1741cm^{-1} in biodiesel produced was the key indicator of successful transesterification, converting triglyceride into ethyl ester [150]. The absorbance monitored were sharp peak indicated the presence of C=O stretching vibration of ester. The comparison between the peaks between the feedstock that was SPO and the biodiesel product was exhibited in Figure 4.15. Similar peaks on most absorbance were observed between these two constituents. It was revealed that stronger and sharper peak at 1741cm^{-1} in biodiesel than at 1735cm^{-1} in SPO feedstock, implying the affirmation concentration of ethyl ester [86]. Production of biodiesel from waste cooking oil from previous studies were reported similar result at this peak [147, 151].

Furthermore, the bending and oscillating vibrations of CH_3 group, possibly from the ester was detected at 1465cm^{-1} peak. Strong peak at 1161cm-1 was typically associated with the ester group stretching vibration (C-O-C) from the formation of ethyl ester [152]. Peak at 1115 cm^{-1} was normally attributed to the existence of C-O ester stretching vibration, identical to previous study [153]. The existence of these similar bands were also been discovered by previous scholar when characterizing biodiesel, produced from waste cooking oil [131]. The appearance of 721cm^{-1} peak in the spectra

was most likely correlated to the rocking of CH_2, similar to study by Abdullah et al. when converting sludge oil to biodiesel [153].

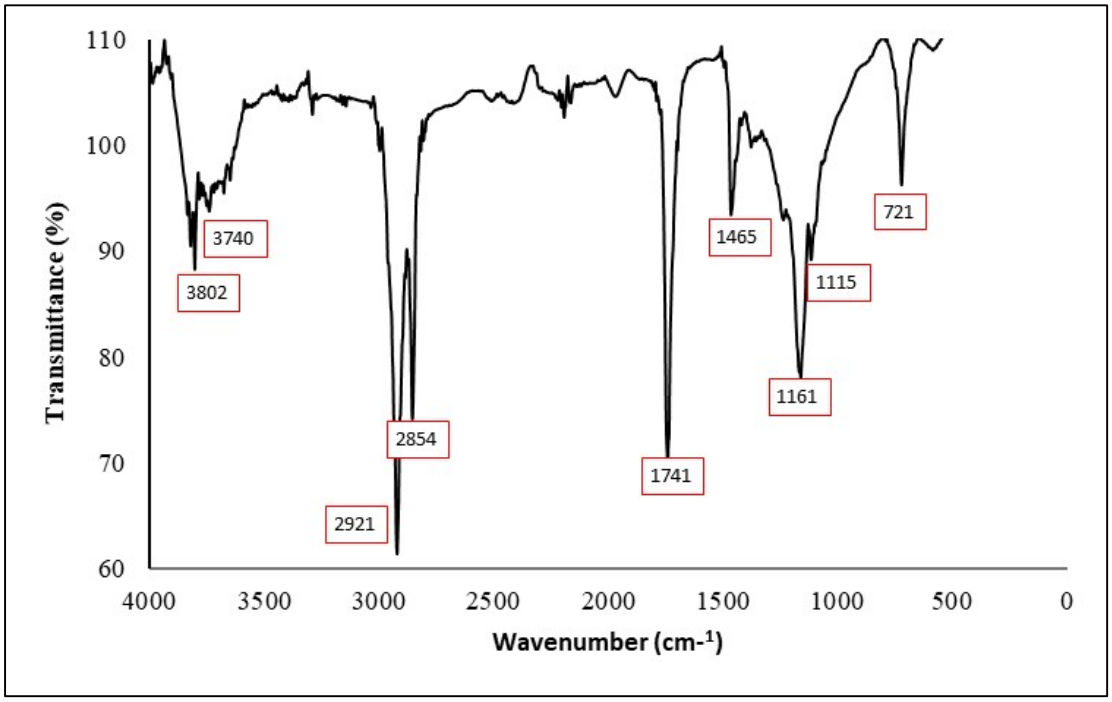


Figure 4.14 FTIR Spectra For Biodiesel Produced.

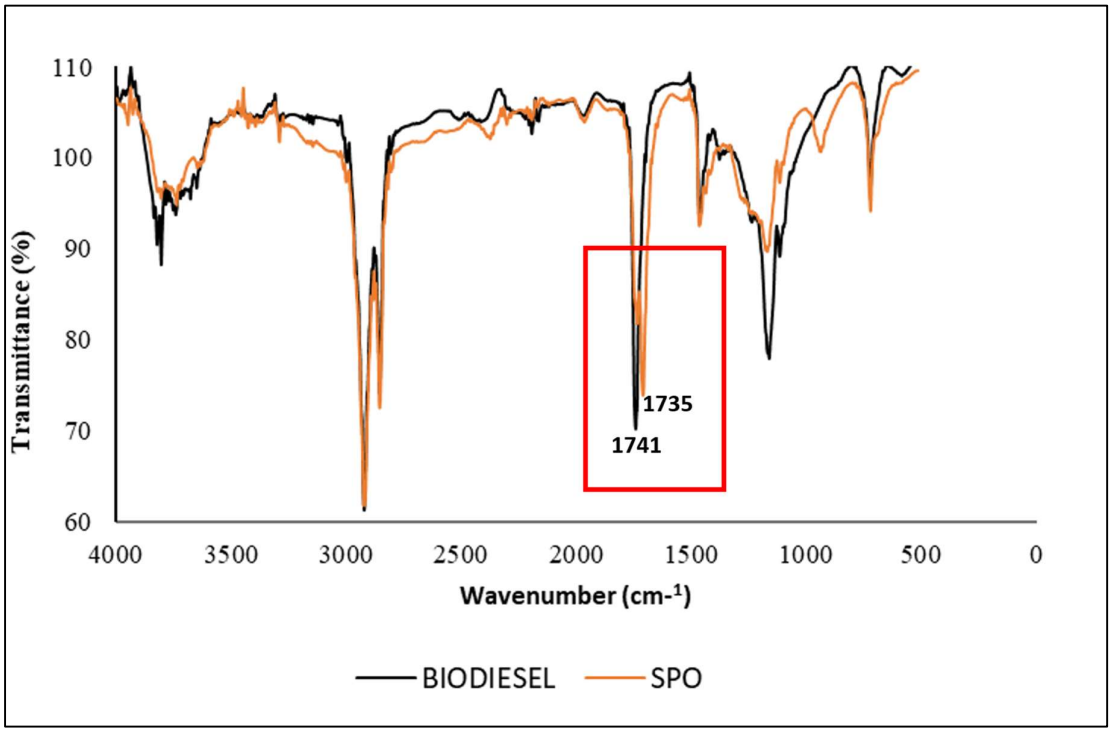


Figure 4.15 Comparison Of The FTIR Analysis For SPO And Biodiesel Produced

Table 4.8
Identification Of The Infrared Spectral Bands Of The Produced Biodiesel In This Study [132, 149, 154].

Wave number (cm^{-1})	Absorption intensity	Functional group identification	Interpretation
3802	Weak, sharp	O-H band	Presence of O-H group from ethanol or glycerol residual
3740	Weak sharp	O-H band	Presence of O-H group from ZnO residual
2921	Strong, sharp	C-H stretching	Presence of C-H groups
2854	Strong, sharp	C-H stretching	Presence of C-H groups
1741	Strong, sharp	C=O stretching	Presence of esters
1465	Strong, sharp	C-H stretching	Presence of C-H groups
1161	Strong, sharp	C-O-C stretching bands	Presence of ester
1115	Strong, sharp	C-O stretching vibration	Presence of ester
721	Strong, sharp	CH_2 rocking	Presence of C-H group

.

To deduce from the FTIR result characterized from the biodiesel produced, it was proven that the formation of ester was performed from the transesterification reaction. The strong peak at 1741cm^{-1} was the common indicator when identifying ester, according to Mohammed et al. [150]. The chemical structure of FAEE was as shown in Figure 4.16. From the peaks observed and interpretation discussion, the appearance of C=O, C-O-C, C-H, CH_3, CH_2 were detected and identified from the spectrum characterized by the produced biodiesel. These finding correlated with the chemical structure of FAEE depicted. Hence, based on this FTIR result, the validation of FAEE produced was implied that the formation of FAEE was achieved.

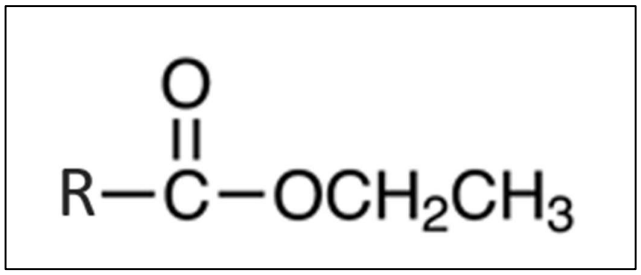


Figure 4.16 Chemical Structure Of Fatty Acid Ethyl Ester

4.7.2 Analysis Of Biodiesel Produced By GC-MS

SPO that has been treated by reducing its FFA content was utilized as the primary feedstock to produce biodiesel by performing transesterification reaction. The analysis of biodiesel produced from the treated SPO was then proceed with the gas chromatography and mass spectroscopy analysis to ascertain the chemical compound and to assess the formation of FAEE in the product. The peaks were analysed by the instrument by comparing the chromatogram with the entries from the CAS library to identify the compound existed in the mixture. The area percentage revealed the total composition for each chemical compound comprised in the content of the produce biodiesel. The chromatogram from the analysis was as portrayed in Figure 4.17. It was reported that component with the same molecular weight, similar fragment patterns, and high SI values (similarity index) to standard compound would be identical.

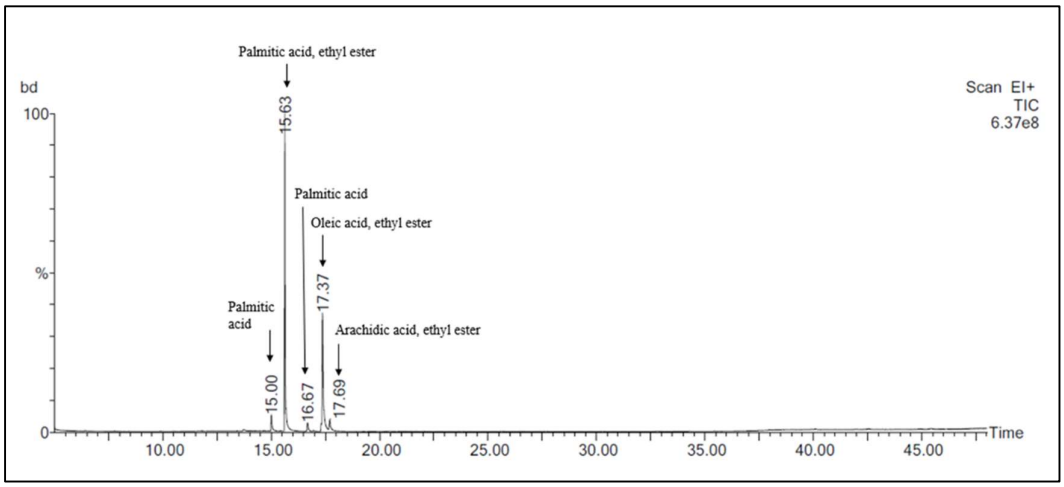


Figure 4.17 GC-MS Chromatogram Of Biodiesel Produced

Referring to Table 4.9, all chemical compound related to the formation of FAEE were listed and it was discovered that the various FAEEs produced peaks were mainly appeared in the total ion chromatogram between 6-to-15-minute retention time. The diverse FAEEs were reflected as the transformation of triglyceride into biodiesel. It was found out that palmitic acid ethyl ester was the majority of the chemical compound that influenced up to 43.456% composition of the produced biodiesel with its retention time of 15.628 minutes. The abundance of palmitic acid in the mixture was established from the fatty acid composition analysis of SPO from previous discussion. Hence, the formation of this fatty acid with the ethanol to produce fatty acid ethyl ester was anticipated, and the analysis from GC-MS proves it. A study from previous report found

14.46% of palmitic acid methyl ester in synthesized biodiesel from the transesterification of seed oil with methanol [150]. The result from the GC-MS analysis implied that the exchange of organic groups between triglyceride and ethanol was performed significantly in the reaction. Triglyceride is a key lipid found in waste oils that composed of glycerol that attached with three molecules of fatty acids. In this study particularly, the primary fatty acid constituted in the triglycerides were palmitic acid, that then been transformed into palmitic acid ethyl ester, from the transesterification process.

Table 4.9
Fatty Acid Ethyl Ester (FAEE) Compound Identified From The GC-MS analysis.

Retention Time (minute)	Compound	Molecular formula	Composition (%)
15.628	Palmitic acid, ethyl ester	$C_{18}H_{36}O_2$	43.456
17.367	Oleic acid, ethyl ester	$C_{20}H_{38}O_2$	22.465
17.693	Arachidic acid, ethyl ester	$C_{22}H_{44}O_2$	2.620
13.731	Arachidic acid ethyl ester	$C_{22}H_{44}O_2$	0.547
6.401	Caprylic acid, ethyl ester	$C_{10}H_{20}O_2$	0.434
		Σ FAEEs	69.522

On the other hand, oleic acid ethyl ester also possesses large value of 22.465% composition of the synthesized biodiesel. Since oleic acid was the second largest composition conspired in the SPO, it was presumed that this fatty acid was abundant in the oil as free fatty acid. When glycerolysis was performed, oleic acid was attached to the introduced glycerol and forming glycerides. The synthesized triglyceride was then undergoing transesterification and producing ethyl ester. As for waste cooking oil as biodiesel feedstock, Sarno and Iuliano reported that oleic acid was the main constituent for its oleic acid methyl ester produced with 63.3% composition on the product [155]. The abundant of both palmitic acid and oleic acid ethyl ester highlighted the dominance of C16 (palmitic acid) and C18 (oleic acid) fatty acids in the SPO produced biodiesel with 44.456% and 22.465% composition, respectively.

Small amount of other ethyl ester with its respective fatty acids were also identified at 17.693, 13.731- and 6.401-minute retention time. Arachidic acid, ethyl ester was detected at both 17.693 and 13.731-minute retention time composing of 2.62% and 0.547% of total composition, respectively. On the other hand, caprylic acid ethyl

ester comprised up to 0.434% composition in the produced biodiesel. These trace of fatty acids in the SPO may reacted with the introduced ethanol to produce its ethyl esters. Although these fatty acid ethyl esters conspired a portion of the composition of biodiesel produced, the primary focus on the production of biodiesel was not to its individual ester, but rather to its overall composition of FAEEs [156]. From the analysis, it can be deduced that the composition corresponded to the formation of FAEE from the treated SPO was conspired of palmitic acid ethyl ester (43.456%), oleic acid ethyl ester (22.465%), arachidic acid ethyl ester (2.62% and 0.547%) and caprylic acid ethyl ester (0.434%). The total percentage composition for fatty acid ethyl ester encountered in the produced biodiesel was 69.522%. This value implied that nearly 70% of the biodiesel produced comprised of fatty acid ethyl ester. According to Sathiyaseelan et al., more than 60% of alkyl ester present in the mixture verified the achievement of the synthesis of biodiesel by transesterification. These esters are the primary components of biodiesel, and their presence confirms the successful of the reaction. However, while 70% FAEE content is a positive sign, biodiesel standards often require a minimum FAEE content of 96.5%, implying the importance to remove the impurities and further purification process to enhance the quality of the biodiesel [157].

From the GC-Ms analysis, chemical components other than FAEE that existed in the product also were detected. The majority of chemical composition present in the SPO biodiesel produced was displayed in Table 4.10 with their respective retention time, and was arranged by the highest to the lowest composition. Components with less than 1% were not stated as they were assumed insignificant. At both 15.001- and 16.674-minute retention time, the compositions of palmitic acid were detected at 3.182% and 1.846%, respectively. When combined, these two contributions yield an overall palmitic acid content of 5.028% in the sample. This revelation is likely due to the unreacted triglyceride in the treated oil. After completion of glycerolysis, a notable reduction in free fatty acids was observed, accompanied by a substantial increase in glyceride formation. Among these glycerides, triglycerides were formed in significant amounts, representing an essential component for biodiesel synthesis. When transesterification was performed, these traces of triglyceride was not reacted to produce the desired FAEE. Hence, the expected minimal amount of this component was observed in the production of biodiesel.

Table 4.10
Chemical Compound Other Than Fatty Acid Ethyl Ester Detected In Produced Biodiesel From GC-MS Analysis

Retention Time (minutes)	Compound	Molecular formula	Composition (%)
15.001	Palmitic acid	$C_{16}H_{32}O_2$	3.182
5.018	Glycerin	$C_3H_8O_3$	2.296
16.674	Palmitic acid	$C_{16}H_{32}O_2$	1.846

Furthermore, the analysis revealed that glycerin was present as a trace component in the product, comprising 2.296% of the total composition. According to the transesterification reaction, triglyceride reacting with alcohol to produce biodiesel as the main product and glycerol is the by-product. Therefore, the justification to the finding of glycerol composition in the mixture was high probably due to the by-product formed from the transesterification reaction. Furthermore, former process of glycerolysis to lower down the FFA in SPO might also contribute to this result. Since the feedstock acquired was the reduced FFA content of SPO with 0.42% of FFA that has been performing glycerolysis with 1:2 SPO to glycerol ratio, the excess glycerol may affect this implication.

The reduced FFA content in the SPO that has been treated by glycerolysis process has significantly enhance the quality of SPO. The formation of fatty acid ethyl esters that were reflected from the GC-MS analysis highlighted the transformation of SPO into biodiesel. SPO that was collected from the waste treatment pond and extremely likely to be discarded as waste was capably to transform into a significant product and a source of global energy. The presence of fatty acid ethyl ester from the GC-MS analysis authenticated the production of biodiesel from the reduced FFA SPO. Hence, the feasibility of SPO as biodiesel feedstock was confirmed and the objective for this study was achieved.

CHAPTER 5
CONCLUSION

5.1 Concluding remarks

Sludge palm oil collected from palm oil mill effluent exhibits chemical characteristics similar to crude palm oil, but contains elevated impurity content and resembles low quality of oil. The FFA value, moisture content and saponification value of SPO was significantly higher than CPO, indicating high degree of deterioration due to its waste attributes. However, SPO still retain fatty acids such as palmitic acid and oleic acid as the principal constituents, making it suitable for biodiesel synthesis. Therefore, it was necessary to treat SPO by reducing the FFA content prior to become the alternative as biodiesel feedstock.

Glycerolysis method was an efficient method offering the formation of triglyceride while reducing the FFA content in the SPO. The study on the effect of different parameters involving temperature, catalyst loading of ZnO and SPO to glycerol mol ratio was able to reduce FFA significantly. Initial value of 59% FFA content in SPO was successfully reduced to 0.42% with 99.3% FFA reduction at 220°C, catalyst loading of 1.0wt% and 1:2 SPO to glycerol mol ratio. This was the lowest FFA value achieved implying the success of glycerolysis method in treating SPO.

The treated SPO with 0.42% FFA was capable of producing fatty acid ethyl ester using ethanol as the reactant indicating the synthesis of biodiesel. The production of biodiesel was affirmed by FTIR and GC-MS analysis. The composition of the final biodiesel product was found to contain a total of 69.522% fatty acid ethyl esters. This significant proportion of FAEEs indicates that the transesterification process was effectively carried out, supporting the conclusion that biodiesel production was successfully achieved using SPO as the feedstock.

Elevated amount of FFA in SPO was significantly reduced by glycerolysis reaction and biodiesel was efficiently produced. The study emphasized the conversion of waste SPO, previously considered a low-value by-product, into biodiesel—an alternative and renewable source of energy—highlighting its potential for sustainable fuel production and waste valorization. The objectives for this study were successfully achieved.

5.2 Recommendation and future perspective

After conducting the study and reaching conclusions, recommendations for future research were outlined as follow:

1. Since there is abundant of SPO sources, SPO with higher value of FFA (more than 59%) should be studied and investigated on its capability to transform into biodiesel.
2. In order to produce biodiesel, treatment of SPO should not be limited to reducing the FFA only, but should take into account other relevant physical characteristics of the oil.
3. To enhance the yield of the biodiesel, further purification of biodiesel produced from treated SPO should be investigated.

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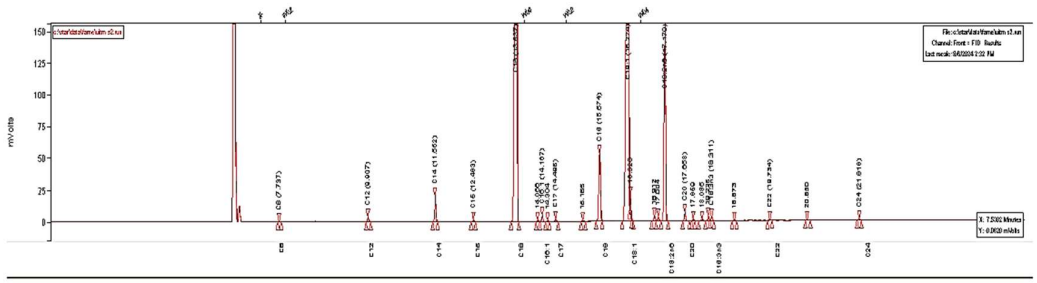
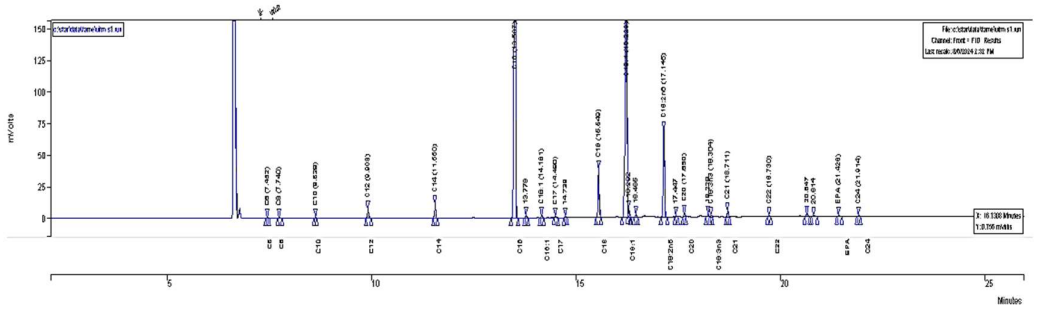
APPENDICES

APPENDIX 1

a.

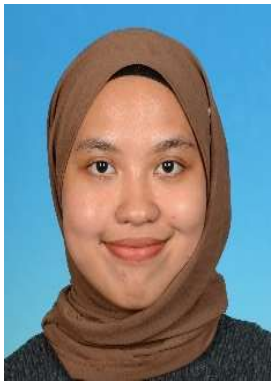


b.



GC-FID analysis for (a) SPO, and (b) CPO.

AUTHOR'S PROFILE



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Farah Nasyitah Esa and Nik Raikhan Nik Him, Treatment of high free fatty acid (FFA) of slude palm oil using glycerolysis method as potential biodiesel feedstock. AIP Conf. Proc, 2025. 3322 (1): 020014

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